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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII OCTOBER 1958 No. 10

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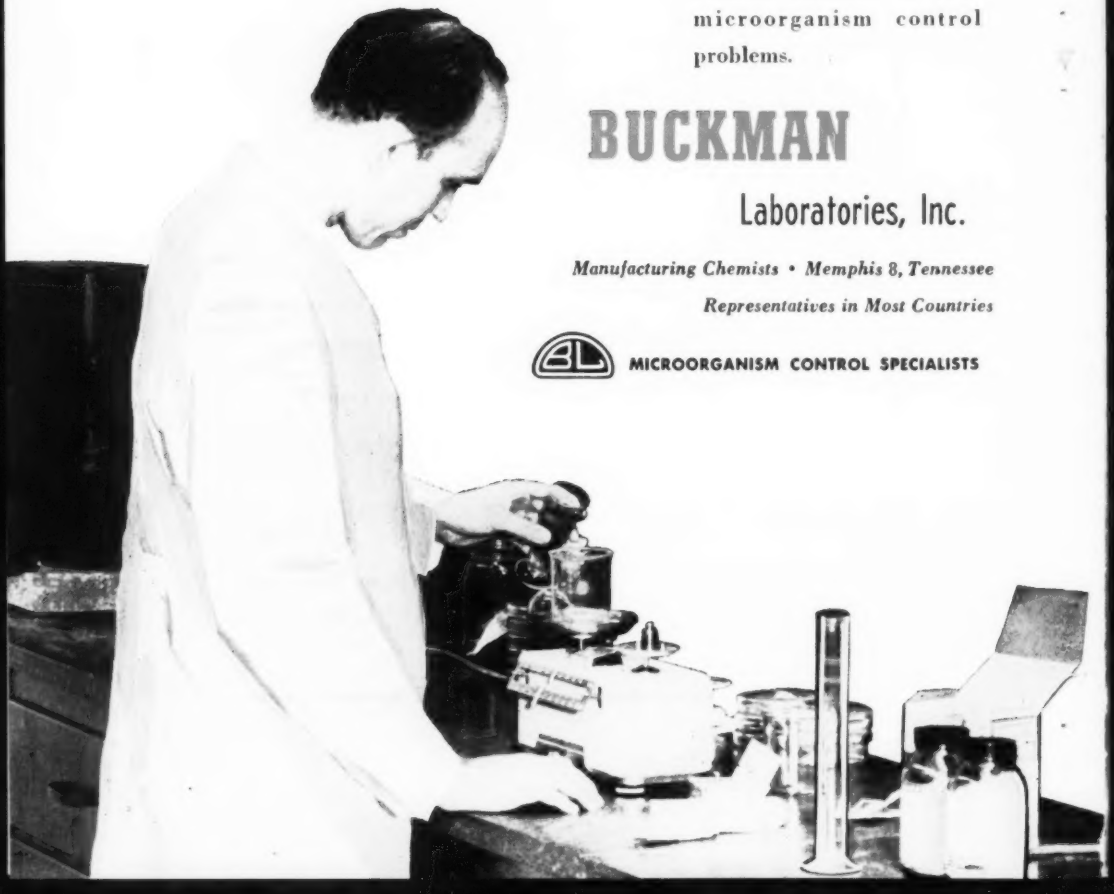

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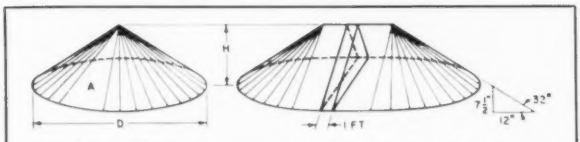

Diagrams of two basic storage piles for rock salt. Conical at left, windrow at right. Note 32° bevel, which applies to both types.

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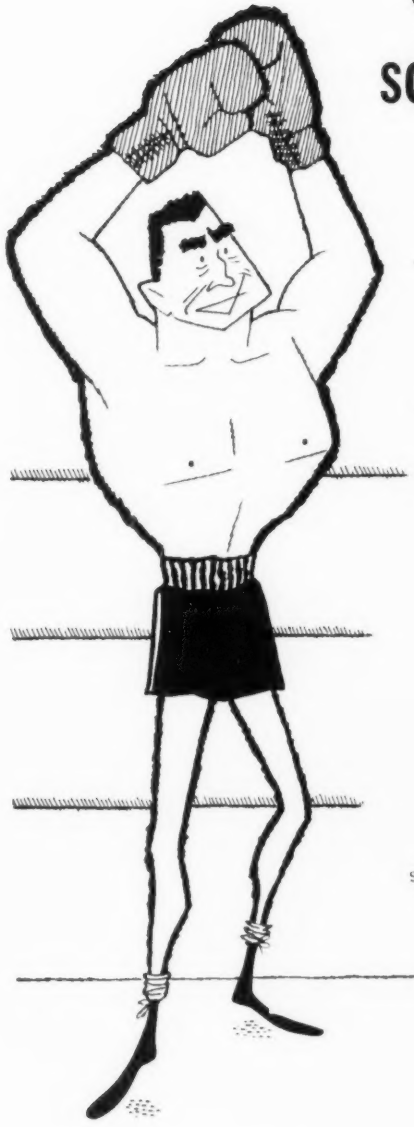

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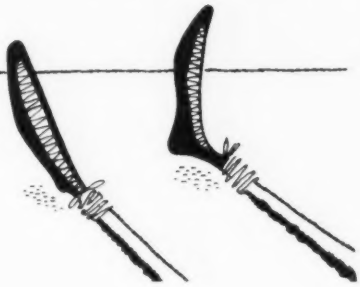

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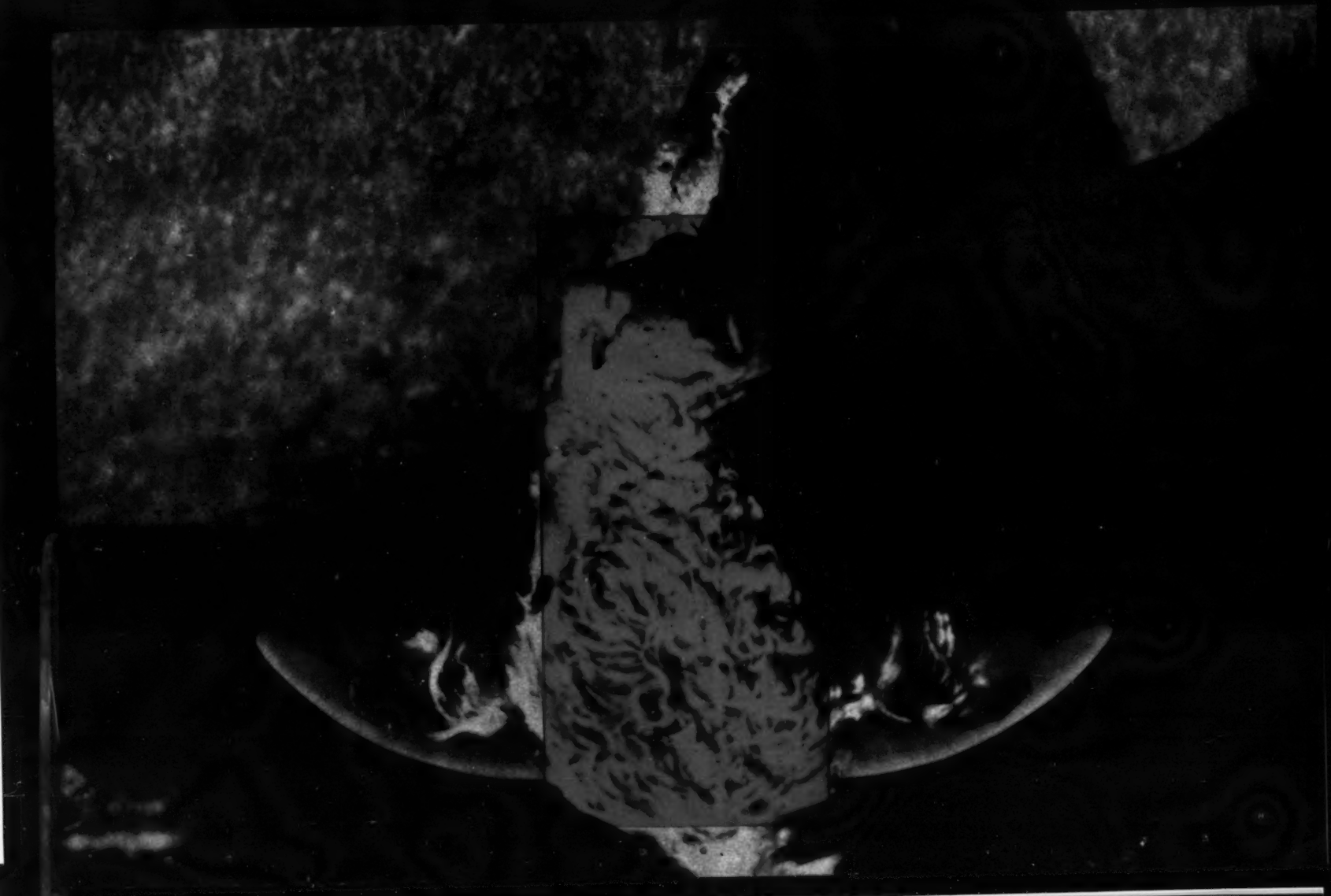

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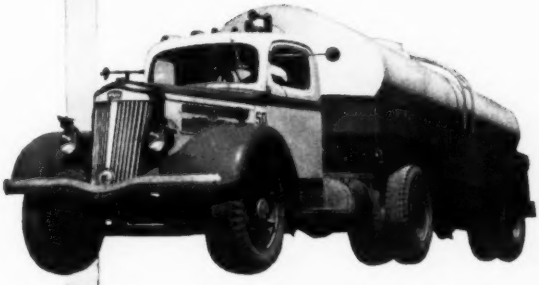

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.

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THE USE OF SALT TO ASSIST ENZYMATIC UNHAIRING OF FRESH HIDES, WITH HISTOCHEMICAL OBSERVATIONS*

ALFRED L. EVERETT AND THEONE C. CORDON

Eastern Regional Research Laboratory†
Philadelphia, Pennsylvania

ABSTRACT

Pretreatment with dilute salt solution had been found advantageous in hastening the unhairing of fresh hides with enzyme. A series of controlled tests was performed to elucidate this relationship between salt concentration in the soak solution and the subsequent rate of unhairing, utilizing a numerical scoring system to interpret the data. The effect of frozen storage of fresh hide was also evaluated in the same manner. Results indicated somewhat different concentration optima for salt treatment, depending upon whether or not the hide had been frozen. Among four staining methods applied to thin sections of salt-treated hide the PAS stain successfully demonstrated changes induced in the basement membrane, while a metachromatic stain made other nearby structures visible.

—x—x—

INTRODUCTION

One of the most common methods of preserving animal skins is treatment with salt. Such treatment prevents the growth of many microorganisms which would otherwise attack and destroy the tissues. Salt treatment also serves other functions. The globular proteins, unwanted for leather-making are solubilized and partially removed. In a series of papers Kritzinger (8–12) reported his studies on the globular proteins of animal skins. He found (10) that 10% sodium chloride was the optimum concentration for removing globular proteins from animal skin and that the concentration of sodium chloride had a marked effect upon the composition of the nitrogenous material extracted. Roddy (18) found that salt extraction of coagulable proteins from a hide or skin while it is still in a freshly flayed condition improves the leather-making properties. Buechler and Lollar (1) used 5% sodium chloride at refrigerator temperature to remove the hair and epidermis from bullhide. By this treatment the entire epidermis could be

*Presented in part at the Fifty-third Annual Meeting of ALCA at Lake Placid, N. Y., June 2–5, 1957.
†Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

taken off in sheets. Cordon (4) found that certain enzymes would rapidly loosen the hair on salt-cured hides but not on fresh hides. This was contrary to the findings of Burton, Reed, and Flint (2). Cordon also found that treatment of fresh hide with dilute sodium chloride made it subject to the action of the hair-loosening enzymes. This paper presents an attempt to evaluate this action of salt solutions by a series of controlled tests and to determine by means of histochemical observations the nature of the changes produced.

MATERIALS AND METHODS

Hides.—The hides used in these studies were heavy steers obtained from a local slaughterhouse shortly after flaying. Hide A, purchased in March, was used for preliminary unhairing tests and for histological study after soaking. Hides B and C, acquired in September and October, respectively, were used entirely for obtaining the unhairing data reported below. All hides were washed with water in a drum, and portions were fleshed and placed in a deep-freeze chest to be thawed as needed. Other similar portions were refrigerated at 34°F. and used within a few days without freezing. Three-inch squares were cut from each hide for the experimental tests.

Enzyme.—The enzyme used was HT Concentrate, produced by the Takamine Laboratories* from a thermophilic bacterium. Its proteolytic and amylolytic potencies as related to its hair-loosening ability have recently been reported (5). Unless otherwise stated it was used at a concentration of 0.1%.

Hide treatments.—Soaking was carried out at room temperature in covered dishes. Hide pieces were completely immersed in solutions containing various concentrations of sodium chloride. For convenience the salt solutions were made up by adding predetermined amounts of salt to one-liter volumes of water, then the concentrations were calculated as grams per 100 grams of solution. Duplicate pieces were removed at daily intervals, rinsed briefly, and placed in 100 ml. enzyme solution held in covered containers in a constant-temperature water bath at 45°C., unless otherwise stated. Phenyl mercuric acetate (0.15 g. per l. solution) was used throughout, both in the soaks and enzyme solutions, to inhibit bacterial growth. At this concentration the compound does not seem to interfere with enzyme action. To obtain maximum protection during prolonged incubation the solution should be replaced every day.

Estimation of hair looseness.—The hide pieces were tested for degree of hair looseness at four 12-hour intervals during incubation by means of a scraping device designed for this purpose (6). The blade was drawn

*The mention of trade names or companies does not constitute an endorsement by the Department of Agriculture over other products of a similar nature not mentioned.

across the hide under constant load in the direction of hair pattern. After ten strokes or less, the approximate percentage of scraped area cleared of hair was estimated visually. Thus a reading of 5-90 means that five strokes removed 90% of the hair and that further attempts were ineffective. Readings of + or ++ indicate slight looseness, as detected by plucking with the fingers, below the threshold of this method. When hair looseness was incomplete (readings poorer than 3-95), the hide pieces were returned to their enzyme solutions for an additional 12 hours and then retested. When adequate loosening was achieved, the pieces were discarded but were scored as complete for any remaining intervals.

Preparation of sections.—Narrow strips were cut from each hide piece after soaking, and placed in 10% formalin (1:10 dilution of U.S.P. formaldehyde solution) for at least two days at room temperature for fixation. Those to be studied were then sectioned vertically on a freezing microtome at 30 to 40 microns. Sections were stored in 50% ethanol to remove formalin and minimize water extraction of soluble components.

Staining methods.—Four different methods were applied routinely to all sections in an attempt to detect changes due to treatment.

1. Periodic acid–Schiff stain (PAS) to demonstrate polysaccharide-containing material. The procedure of Hotchkiss (7) using alcoholic reagents was found preferable. This method, with suitable controls, is said (17) to be specific for 1, 2-glycols or amino-glycols and certain lipoids, which are oxidized to dialdehyde by periodic acid and made visible with Schiff reagent.

2. Crystal violet stain to show globular proteins. This was essentially the method used by Roddy (18) in his study of coagulable proteins. Diffusion of the stain occurs rather rapidly, so that slides must be examined or photographed within one day to give valid results.

3. Toluidine blue to stain nuclei orthochromatically (blue to purple) and acid mucopolysaccharides metachromatically (pink to red). Dilute dye was used (15) in McIlvaine buffers at pH 2, 4, 6, and 8. Sections were then rinsed rapidly, dehydrated, cleared, and mounted in balsam. Several good reviews (17, 19) are available to explain the theory of metachromasia and to help interpret results.

4. Alcian blue–PAS stain to show differentially various mucins and polysaccharides. The procedure was basically according to Steedman (13, p. 287) as modified by Mowry (16). Acidified dye was used, followed by alkaline fixation and then the complete PAS procedure. The blue and red colors provide a very effective contrast.

RESULTS AND DISCUSSION

In previous studies on the effect of salt treatment of fresh hide on hair loosening by enzymes, it had been consistently found that preliminary soaking in 2% to 8% NaCl was necessary to permit proper loosening with enzyme. If the hide was unsoaked, or soaked in plain water or strong salt, it exhibited considerable resistance to enzyme action. Also it was confirmed that dilute salt solution had a slow unhairing action by itself (3 to 5 days). In this case the hair-loosening action was too slow for commercial application but was of interest because almost the entire epidermal system could be removed intact. Figure 1 shows a photograph of the underside of this epidermal layer.

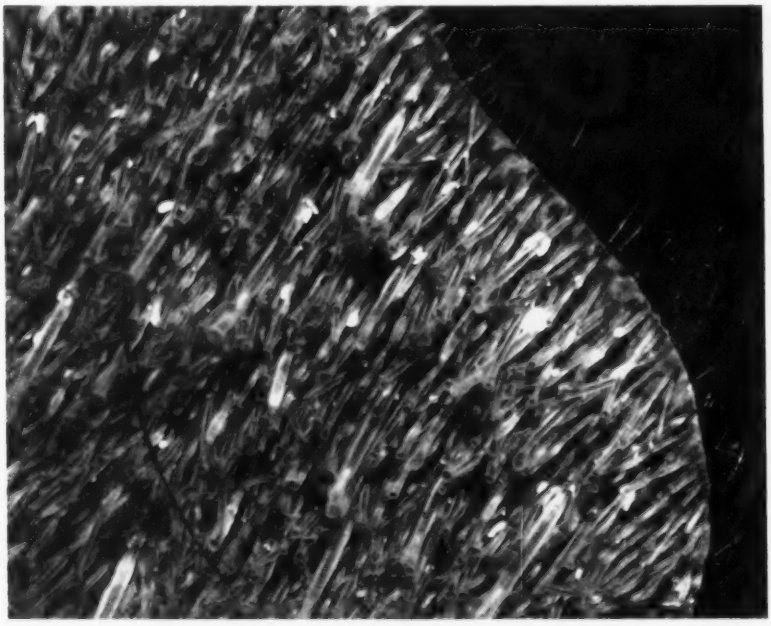

FIGURE 1.—Enlarged view of epidermis, with hairs and glands attached, removed from frozen hide after soaking for 5 days in 5% salt solution.

All of this work had been done with fresh hide held in the frozen state for varying periods. Preliminary experiments for this report employed hide that had been held frozen for over six months, using salt soaks over the range 0% to 20%. With this material the enzymatic unhairing was uniformly rapid in each case, showing no difference whatever due to pretreat-

ment. Since no other reasonable explanation could be found, it was deduced that there might be a definite effect on the hide due to frozen storage that could alter its response to enzyme. In a recent study Cooper and Sykes (3) have shown that freeze-drying of fresh hide causes irreversible changes which prevent complete rehydration of the hide, with evidence of denaturation of both globular proteins and mucopolysaccharides. Consequently three additional fresh hides were obtained over a period of time to test separately the effects of freezing and salt-soaking on the rate of enzymatic unhairing.

Tests with fresh nonfrozen hides.—No unhairing data are presented here for hide A since only a few replicates were run. However, two other hides (referred to elsewhere as hide B and hide C) were compared in several ways, both as nonfrozen and frozen material. Table I illustrates a representative experiment to determine the relative effectiveness of pretreatment with various levels of salt in enhancing the rate of unhairing by 0.1% solutions of enzyme. This concentration of enzyme was purposely rather weak in order to bring out differences between treatments. The scoring system, shown in the last two columns, was derived as follows: An arbitrary end point for readings of hair looseness (3–95) was chosen to represent a degree of looseness just short of absolute completion (1–100). Whenever this end point or a reading closer to absolute completion was reached during examination of a hide piece, the letter X was added to the reading recorded in one of the four center columns, to denote scoring of one point. The hide piece was then discarded but was still scored as completed for any remaining time intervals. By adding these points horizontally for each pair of duplicates one obtains the numerator for the fraction recorded in the next to the last column. The denominator is merely the maximum possible score. Note that this denominator when divided by four indicates the number of replicates involved. The last column expresses this fraction as a whole number for comparative purposes.

Table II summarizes the data for both hides obtained from a number of similar tests. Because of the large variability between hides as well as between pieces of the same hide the composite scores gave the best picture of the effect of treatment with solutions of varying salt concentrations. It can be seen that soaking for two days was always a little better than for one day. Data were also recorded after three days (and sometimes after four and five days) but did not seem significantly different and consequently are not shown. Also there was a pronounced peak in activity after soaking in 4.8% salt, which confirmed previous experience (4). However, this peak did not recede much with increase in salt concentration, but rather a secondary higher peak was shown at the saturation point. This result was quite unexpected. Controls without enzyme consistently showed negligible looseness, whether incubated in water at 45°C. or in the various salt solutions at room temperature.

TABLE I

REPRESENTATIVE EXPERIMENT SHOWING EFFECTS OF SOAKING IN SALT SOLUTIONS ON RATE OF ENZYMATIC UNHAIRING OF NONFROZEN FRESH HIDE

Soak Conditions		Hair Looseness Readings, 45°C				Unhairing Results	
NaCl	Days	12 hr.	24 hr.	36 hr.	48 hr.	Score	Score × 100
%		P* R†	P R	P R	P R		
0	1	0‡	+–++	10–90	3–98X		
		0	+–++	10–80	3–98X	2/8	25
	2	+–++	3–98X**	X	X		
		0–+	5–95	3–98X	X	5/8	63
1.2	1	++	5–95	3–98X	X		
		10–60	6–98	3–100X	X	4/8	50
	2	0–+	10–90	2–98X	X		
		++	7–95	3–98X	X	4/8	50
2.4	1	10–80	5–98	3–98X	X		
		++	7–95	3–98X	X	4/8	50
	2	0–+	3–98X	X	X		
		++	6–95	3–100X	X	5/8	63
4.8	1	10–70	3–98X	X	X		
		10–80	3–98X	X	X	6/8	75
	2	++	3–98X	X	X		
		++	5–98	3–98X	X	5/8	63
9.1	1	+–++	5–95	3–98X	X		
		+–++	5–90	3–98X	X	4/8	50
	2	7–98	4–100X	X	X		
		6–98	3–100X	X	X	6/8	75
16.7	1	+	5–98	3–98X	X		
		+–++	4–98	3–98X	X	4/8	50
	2	0	5–95	3–98X	X		
		4–95	4–100X	X	X	5/8	63
25.9	1	+	4–98	3–98X	X		
		+–++	3–98X	X	X	5/8	63
	2	0	3–98X	X	X		
		0	3–98X	X	X	6/8	75
No Soak		0	++	6–98	3–98X		
		++	6–95	3–98X	X	3/8	38
No Enzyme		0	0	0	+		
		0	0	0	0	0/8	0

*Number of pulls with scraper (see Methods section).
†Estimated percent of hair removed from scraped area.
‡0 = hair tight; + and ++ = slight looseness not measurable by scraper.
**Symbol X denotes point scored for reaching end point (3–95 or better.) Add points horizontally for each duplicate pair to obtain score numerator; denominator is maximum number possible.

Effect of lower temperature. In a series of similar tests the incubation temperature for enzyme treatment was lowered from 45° to 40°C. No significant change was seen in the unhairing scores obtained; all values were somewhat lower but within about 7% of those shown in Table II.

TABLE II

SUMMARY OF UNHAIRING* SCORES† FOR NONFROZEN PORTIONS OF TWO FRESH HIDES

Soak Conditions		Hide B		Hide C		Composite		
% NaCl	No. Days	Score	Score × 100	Score	Score × 100	Score	Score × 100	Average
0	1	7/12	58	6/16	38	13/38	46	52
	2	6/12	50	10/16	63	16/28	57	
1.2	1	6/12	50	9/16	56	15/28	54	56
	2	7/12	58	9/16	56	16/28	57	
2.4	1	6/12	50	9/16	56	15/28	54	63
	2	9/12	75	11/16	69	20/28	71	
4.8	1	20/28	71	10/16	63	30/44	68	70
	2	9/12	75	11/16	69	20/28	71	
9.1	1	6/12	50	10/16	63	16/28	57	66
	2	9/12	75	12/16	75	21/28	75	
16.7	1	8/12	67	9/16	56	17/28	61	66
	2	8/12	67	12/16	75	20/28	71	
25.9	1	16/20	80	11/16	69	27/36	75	82
	2	16/16	100	12/16	75	28/32	88	
No Soak	–	6/12	50	7/16	44	13/28	46	
No Enzyme	–	0/12	0	0/16	0	0/28	0	

*Treated with 0.1% HT Concentrate at 45° C.
†Scoring system explained by Table I.

TABLE III

SUMMARY OF UNHAIRING* SCORES† FOR FROZEN PORTIONS OF TWO FRESH HIDES

Soak Conditions		Hide B		Hide C		Composite		
% NaCl	No. Days	Score	Score × 100	Score	Score × 100	Score	Score × 100	Average
0	1	21/28	75	9/16	56	30/44	68	67
	2	12/16	75	9/16	56	21/32	66	
1.2	1	21/28	75	9/16	56	30/44	68	70
	2	13/16	81	10/16	63	23/32	72	
2.4	1	21/28	75	9/16	56	30/44	68	70
	2	13/16	81	10/16	63	23/32	72	
4.8	1	20/28	71	9/16	56	29/44	66	74
	2	15/16	94	11/16	69	26/32	81	
9.1	1	25/28	89	11/16	69	36/44	82	82
	2	16/16	100	10/16	63	26/32	81	
16.7	1	28/28	100	11/16	69	39/44	89	87
	2	15/16	94	12/16	75	27/32	84	
25.9	1	22/24	92	11/16	69	33/40	83	83
	2	3/8	100	12/16	75	20/24	83	
No Soak	–	26/36	72	9/16	56	35/52	67	
No Enzyme	–	0/24	0	0/16	0	0/40	0	

*Treated with 0.1% HT Concentrate at 45° C.
†Scoring system explained by Table I.

Effect of adding salt to enzyme solutions. It was thought that perhaps the time required for soaking could be eliminated by adding low levels of salt directly to the enzyme solution and performing both functions simultaneously. A number of concentrations, from 0% to 20%, were tried in several tests with both hides at 45°C. In general the scores remained at least 10% below the first peak of activity shown in Table II; therefore this procedure was not as effective as preliminary soaking. In fact there was strong inhibition of activity with increasing salt content, starting at about 5%. Some evidence of weak stimulation was apparent with 1% NaCl (normal physiological level in living tissue). Controls without enzyme began to show very slight hair loosening in four days with salt concentration below 5%, but none above this point.

Tests with hides preserved by freezing.—The data summarized in Table III and which may be compared directly with Table II were obtained by using portions of hides B and C that had been held frozen for periods up to one month. It is apparent that in this series there was a much greater difference between hides than was noted before, since hide C consistently showed lower scores than hide B. Also there was very little, if any, advantage in soaking for two days rather than one. Results after soaking for three days, not shown, were more typical in giving higher scores for each treatment. It should be noted here that after soaking for two, and especially for three days, in the three weakest salt solutions, it was common to observe appreciable hair looseness (++) with frozen hide. This did not occur with the hide which had not been frozen. The average unhairing scores from Tables II and III were plotted for comparison in Fig. 2. Here it can be seen that hide which had been frozen always unhaired a little faster than that which had not been frozen. Also the two activity peaks in the curve for nonfrozen hide are clearly evident, while the curve for frozen hide has just one peak, between 10% and 20% salt. As time of frozen storage is extended this latter curve tends to level off. In seeking an explanation for this beneficial action of frozen storage it might be considered as another manifestation of the salt effect. Lovelock and others (14, and following papers in the same issue) have pointed out that during slow freezing of a tissue there is a gradual increase in the formation of ice crystals in the intercellular spaces. This removal of water results in a corresponding increase in the concentration of electrolytes dissolved in tissue fluids. It is conceivable that the concentration could reach effective levels and that the effect could increase with time.

Effect of lower temperature. In a series of similar tests the incubation temperature was changed from 45° to 40°C. as described for nonfrozen hide. Again there was no significant change in scores due to change in temperature, and the general response to conditions of soaking remained the same.

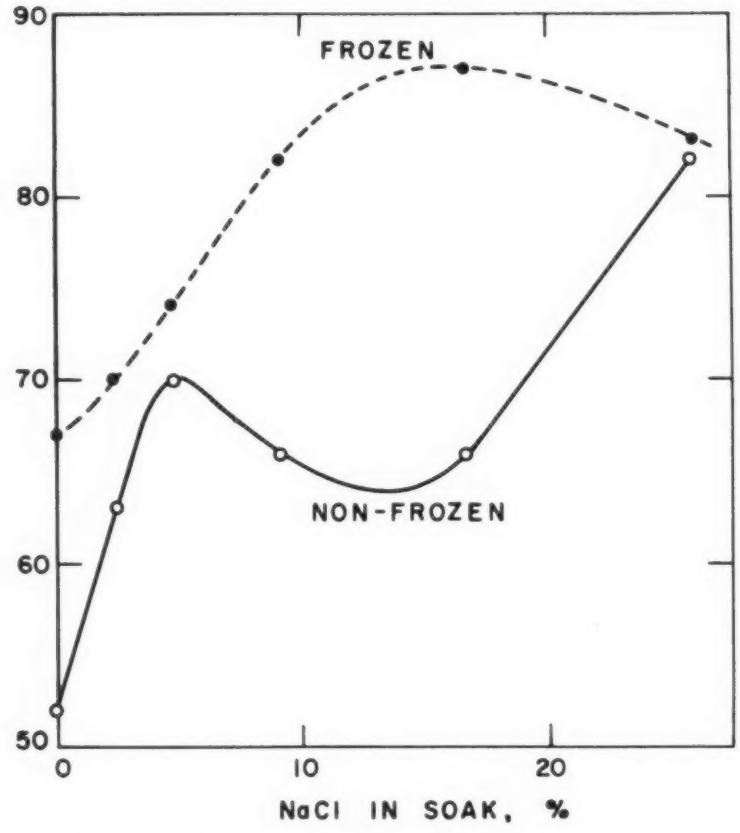

FIGURE 2.—Influence of salt concentration in the soak on the rate of unhairing of frozen and nonfrozen cattlehides with 0.1% HT Concentrate at 45° C.

Effect of stronger enzyme. In a short series of tests 0.2% enzyme was substituted for 0.1% at 45°C. Unhairing scores averaged about 10% higher in almost every instance but otherwise showed the same general response to soaking treatment.

Effect of adding salt to enzyme. A series of tests with various levels of salt added directly to the enzyme solutions was carried out as described above for nonfrozen hide. Again the frozen hide behaved in a similar manner to that which had not been frozen—there was weak stimulation at around 1% NaCl (however, the best score was more than 10% below the first ac-

tivity peak shown in Table III), and the same pattern of inhibition resulted with higher levels of salt. When 0.2% enzyme was used in place of 0.1%, the same general results were obtained except that the increase in inhibition was more gradual and did not become pronounced until about 9% salt concentration.

HISTOLOGICAL AND HISTOCHEMICAL STUDIES

In order to obtain additional information on the changes induced in hide components by salt treatment, sections from soaked nonfrozen hide pieces were subjected to various histochemical procedures and examined microscopically. Also an attempt was made to record some of the results photographically for reference purposes. It is understandably difficult to render in black and white the many shades and hues of a stained tissue and to achieve good focus with relatively thick sections. Therefore it is apparent that more information was gained from direct microscopic examination than can be shown in black and white prints. Nevertheless a few photos are included to help illustrate the results.

PAS stain.—It was expected that the PAS stain might prove the most informative, since it makes visible polysaccharide-containing materials including mucopolysaccharides, mucoproteins, and glyco-proteins. One or more of such components are known to be present in the grain layer and might well be the principal substrate concerned with hair loosening. When fresh, untreated hide was stained by this method (Fig. 3), the most prominent structure visible was an intense red band, of variable thickness depending upon the orientation of the cutting plane, immediately below the base of the epidermis. This is commonly referred to as the basement membrane, but the stained band probably includes more than the membrane proper. It appears to include also the uppermost zone of collagenous dermis, so modified as to contain a cementing substance, rich in polysaccharide, for holding the epidermis in place by means of minute extensions of the basal cells. Muscular tissue was also strongly stained, while a lighter shade appeared in the epidermal cytoplasm, the background of dermis (ground substance), and the thicker elastin fibers. It had been observed that treatment of hide with HT Concentrate removed practically all trace of the bright red band. Therefore, it seemed logical to examine this structure for any changes brought about by soaking in various salt solutions, since these treatments were shown to affect the rate of unhairing. Soaking in water (Fig. 4) did not seem to alter the appearance of the basement membrane, although the background staining in both dermis and epidermis was less intense. However, after the hide was soaked in 4.8% salt (Fig. 5), the picture was quite different. The stained band in the dermis was broader and much less intense, while the basal layer of epidermis remained rather dark, and there was gross separation between

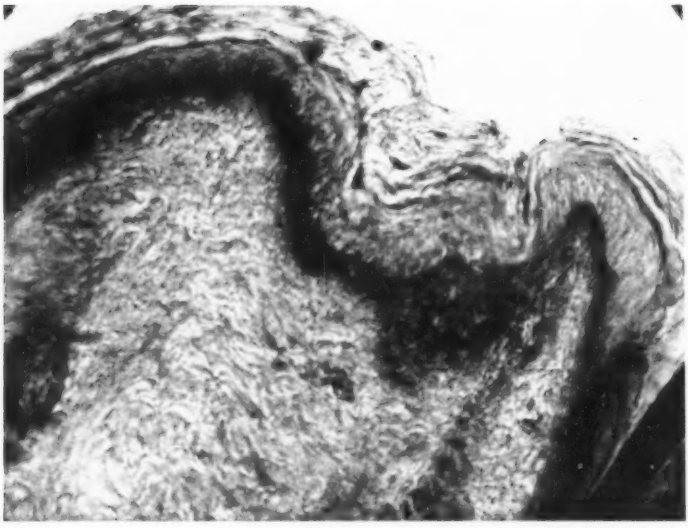

FIGURE 3

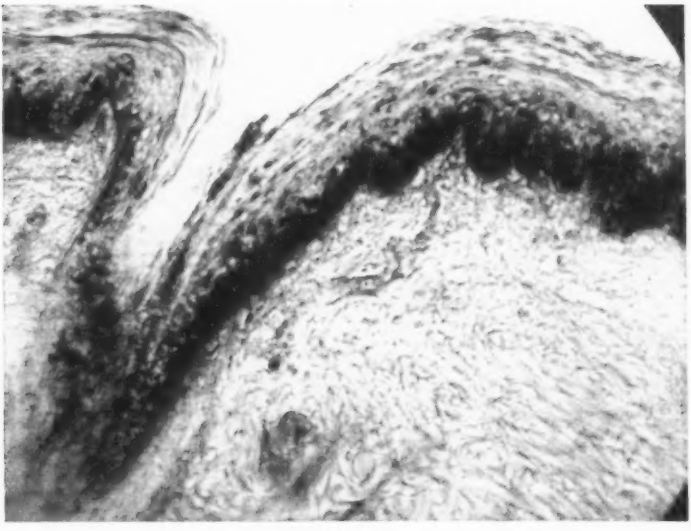

FIGURE 4

FIGURES 3–4.—Cross sections, nonfrozen fresh hide, PAS stain, green filter. ×200.
Figure 3.—Untreated. Figure 4.—Soaked in water.

FIGURE 5

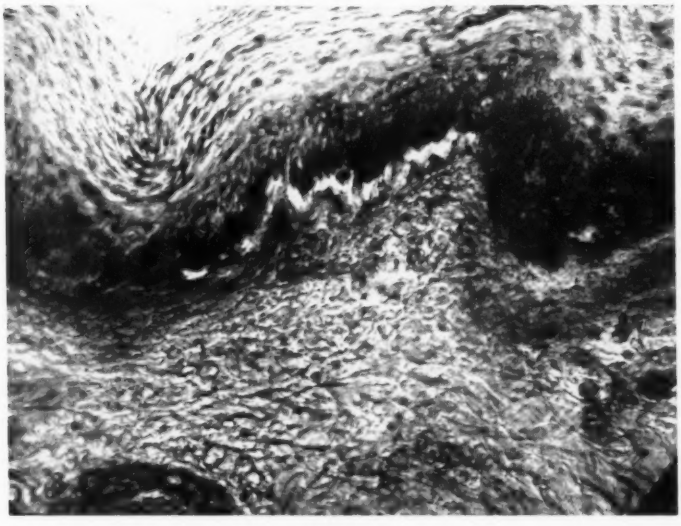

FIGURE 6

FIGURES 5–6.—Cross sections, nonfrozen fresh hide, PAS stain, green filter. ×200.
Figure 5.—Soaked in 4.8% salt. Figure 6.—Soaked in 9.1% salt.

FIGURE 7

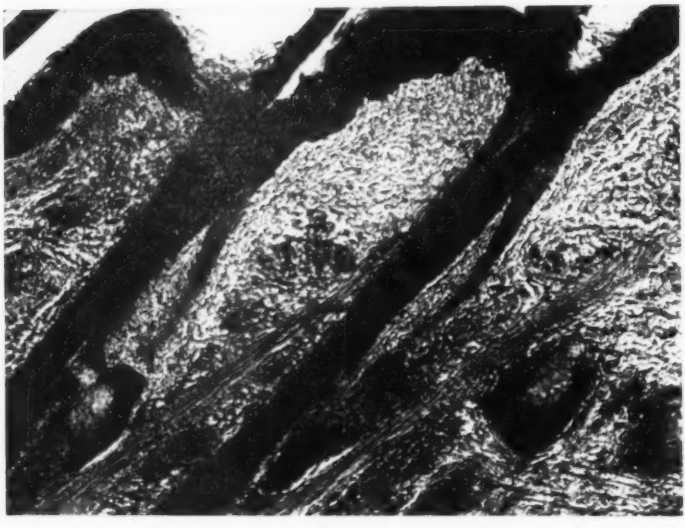

FIGURE 8

FIGURES 7–8.—Cross sections, nonfrozen fresh hide, crystal violet stain, yellow filter. ×100. Figure 7.—Untreated. Figure 8.—Soaked in 4.8% salt.

FIGURE 9

FIGURE 10

FIGURES 9–10.—Sections of nonfrozen fresh hide, stained with toluidine blue at pH 6, green filter. ×100. Figure 9.—Untreated. Figure 10.—Soaked in 4.8% salt.

the layers in many places. Similar changes, to a lesser degree, were noted after the hide was soaked in 2.4% salt. This apparently represents an early stage of unhairing, which is then brought to rapid completion by the enzyme. Soaking the hide in 9.1% salt (Fig. 6) gave a similar result (and a somewhat clearer photograph), although epidermal separation is not usually as extensive with strong salt solutions as it is with dilute ones. Note the abnormally thick epidermis in this sample—a frequent observation with this hide.

Crystal violet.—Some effects of pretreatment were also detected with the crystal violet stain, which was intended to make visible globular proteins. Freshly stained untreated hide (Fig. 7) showed intense coloration of all cellular elements such as epidermis, glands, blood vessels, and muscles. In addition there was moderate background staining throughout the grain layer but much weaker in the corium. Soaking the hide in water caused a pronounced reduction of stain intensity, especially in the epidermis. The weaker salt solutions (Fig. 8) did not seem to affect the cellular staining to any appreciable extent. However, there was a gradual but progressive reduction in the staining of the background of the grain as the salt content increased, while the corium became completely devoid of staining materials. The maximal effect appeared to be reached at 9.1% salt concentration, since a slight reversal occurred at the highest salt levels. Although these results showed no direct correlation with subsequent unhairing behavior, they do indicate that globular proteins are not prominent in the basement membrane but probably are more important in relation to tanning operations.

Metachromatic stain.—Staining with metachromatic dyes such as toluidine blue produced some striking color contrasts in hide sections. In fresh untreated hide the cell nuclei, and to some extent the cytoplasm of growing epidermis, appeared purplish blue, the natural color of the dye. However, in certain characteristic locations there were variable amounts of material that stained metachromatically in shades of pink to red. Staining at pH 4 to 6 was optimal for this purpose. The most noticeable locations where this appeared were the loose connective tissue around the capillary network of the upper grain layer, the sebaceous glands, the lower half of growing follicles, and the papillae of growing hairs. Also, in specialized cells of the upper grain layer called mast cells, the cytoplasm was filled with red metachromatic granules. Collagen and elastic tissue remained unstained, and the *stratum corneum* or top dead layer of epidermis was pale green. A section of the untreated fresh hide stained by this method at pH 6 is shown in Fig. 9; however, the pink and red areas are represented in this photograph by corresponding tones of medium to dark gray. Mast cells are the large dark spots scattered through the upper dermis. Montagna *et al* (15)

have shown some excellent color plates of metachromasia in growing hair follicles, which they associate with the process of keratinization.

When hide pieces had been soaked in dilute salt solutions (Fig. 10), there appeared to be no change in the metachromatic materials of the dermis, but the delicate violet shade (apparently due to both blue- and pink-staining elements) in the lower epidermis was lost. Soaking in water or strong salt caused osmotic disruption of the mast cells. Also it seemed that treatment with 9.1% salt or stronger reduced the intensity of the pink zones of the capillary beds. After treatment with the unhairing enzyme the tissues became devoid of metachromatic staining material. These findings indicate that the basement membrane apparently contains no sulfated mucopolysaccharides, but such materials are removed from the other tissues by the unhairing enzyme.

Alcian blue PAS.—Alcian blue was also used to demonstrate mucins or mucoids. It was found to be specific for the same structures stained by toluidine blue but without metachromatic properties, since it produced only shades of blue. The color formed, however, is very resistant to chemical reagents, which permits counterstaining by procedures such as PAS. Although it has yielded no new information, it served to confirm results obtained with the other staining procedures.

SUMMARY

Results have been presented from a number of experiments to determine the relative effectiveness of various salt pretreatments in stimulating the rate of unhairing of fresh hides with a commercial enzyme. Parallel tests were also included to evaluate the additional factor of frozen storage of the hide. It was found that frozen hide always unhaired faster than nonfrozen hide after the same pretreatments. Plotting the rate of unhairing as a function of salt concentration in the soak solutions revealed that nonfrozen hide responded with two activity peaks, the first at about 5% salt and the second, a stronger one, at about 26% salt (saturated). With frozen hide there was only one broad peak, between 9 and 26% salt. Soaking the hide for two or three days caused faster unhairing than soaking for one day. There was no definite advantage in adding salt to the enzyme solution in place of preliminary soaking in salt solution, nor was there any real difference in results whether the enzyme solution was incubated at 40° or 45°C.

Histochemical evidence suggested several possible effects of salt pretreatment. The PAS stain, broadly specific for polysaccharide components, demonstrated a prominent structure referred to as the basement membrane (junction of dermis and epidermis) which is apparently the principal site of unhairing action. Treatment with certain salt solutions altered the

appearance of this layer and caused preliminary separation of the epidermis. Staining with crystal violet indicated that globular proteins are not an important constituent of this region but are subject to salt extraction. Metachromatic staining, said to be specific for acid mucopolysaccharides, failed to make the basement membrane visible but gave positive results in other locations, some of which were altered by salt treatment. Alcian blue helped to confirm these results.

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DISCUSSION

DR. JULIUS PFANNMULLER (Wallerstien Company, Inc.): We thank Dr. Cordon for a very interesting paper. I think Dr. Cordon's paper looks into the future. As far as I know, the tanners are quite dissatisfied with chemical

methods in unhairing hides and skins and are looking towards enzymatic methods. Whether such enzymatic methods will ever be realized on a large scale, we do not know. Of course, we all hope they will, because the problem of sewage disposal would be much easier. And this is a problem in practically every country.

As to the influence of salt on enzyme unhairing, the influence of salt on chemical unhairing of skins is known. We know that it dissolves certain globulins. Generally we might say that salt interferes in chemical unhairing of skins with lime. High salt concentration in enzymatic unhairing should also interfere. However, according to this paper, it seems that a small addition of salt aids enzymatic unhairing.

Now we have to see the practical side of enzymatic unhairing. Enzymatic unhairing in this country was carried out on a large scale on goatskins. But according to Dr. Cordon, the technical process was only carried out by first swelling the skins with caustic and then unhairing with enzymes.

I think Dr. Cordon carried out his unhairing experiments on skins that were not pretreated with any caustic materials. He did not use a pure single enzyme but rather enzyme mixtures. We probably could get more fundamental knowledge if we would work with pure enzymes. The best would be to use crystalline enzymes.

On the other hand, pure enzymes are very expensive, so enzyme mixtures will be used for technical unhairing. According to the findings of Dr. Cordon, there was a very big difference in unhairing skins that had been kept six months in cold storage. Now certainly, certain mechanical destruction of the structure of the skin caused by water crystallization should be expected. Salt showed no influence in unhairing hides after six months storage. Probably some mechanical destruction of the fiber structure allowed the enzyme to penetrate more easily.

I wish that some people here would tell me a little about enzymatic unhairing. I hear that it is now carried out in Europe with high concentrations of enzymes without previous swelling of the skin. They take hides where the salt is thoroughly washed out. They use practically no water. Later, for easier mechanical unhairing, they swell the hides with a little caustic. That is just about the opposite of what was formerly done in the enzymatic unhairing process—the one used in this country for unhairing goatskins.

DR. L. T. KREMZNER (General Foods Corp.): I would like to bring to the attention of the speaker some recent work reported by a Dr. Nickerson of Rutgers University and the Institute of Microbiology. He has reported on a microorganism which secretes keratinase, and this keratinase will, in a couple

of hours, dehair a hide. That is all that I know about it now, except that I do understand that there will be a commercial process in a short time—that is, the manufacture of the enzyme.

DR. CORDON: I know of Dr. Nickerson's work at Rutgers, having seen an abstract of a paper he presented about a year ago. I believe he described some keratinase enzymes. I wrote to him for some of his cultures, but he did not answer my letter.

We have in mind work along that line, to investigate certain purified enzymes to see their effects on specific components of the hide.

DR. PFANNMULLER: I might add something: We have two basicly different unhairing principles. Unhairing with the proteolytic enzymes undoubtedly is due to a proteolytic action. The keratinase unhairing action is probably due to a disulfide reductase enzyme, so this enzymatic action should be similar to that occurring in lime with sharpness. The disulfide reductase should break the disulfide links of the keratin, an action similar to that occurring in a chemical unhairing process. Disulfide reductases from an enzymatic standpoint are difficult to obtain and to determine exactly.

DR. H. G. TURLEY (Rohm & Haas, Philadelphia, Pa.): I can contribute nothing to the matter just discussed. However, on the subject of enzymatic unhairing, it looks like the pendulum is swinging back again. Forty years ago or so, there was great interest in that, and there was a certain amount of success achieved. Then I think we can safely say that it died out substantially.

My own feeling about the matter is that this type of process requires too much direction and study, and so forth, for the usual tanner. Times have changed, however, and we have better personnel who have more knowledge and more equipment, and now we also have the problem of sewage disposal, so enzyme unhairing has come up again. It has cropped up, I think, due to the work recently done in Great Britain. I can say it is sufficiently interesting in Europe that at the forthcoming meeting in Rome there will be about four papers on enzyme unhairing, and I think from about four different countries. One of them is concerned with enzyme unhairing using proteolytic complexes of streptomyces.

I saw one of Dr. Cordon's slides, and it showed the detachment of a portion of the epidermis. But curiously enough, the detachment did not extend into the hair roots. It is the same type of material. Does Dr. Cordon have any ideas about that?

Secondly, I think the sections would have been a little easier to see had there been better differentiation. They were rather heavily stained, and I don't know how much consideration has been given to the technique of the art. When that is treated carefully, we can usually see more.

DR. CORDON: As to the first question, Dr. Turley, the entire epidermis is loosened by salt-soaking including the sebaceous glands and hair follicles. This was shown on a slide before you came in.

As to the second question—thank you, we will try to improve our technique.

DR. PFANNMULLER: Do you think there could be two enzymatic unhairing methods—first, one with proteolytic enzyme systems, and another one similar to the chemical method with enzyme systems that break down disulfide links?

DR. TURLEY: It might be possible, although we do not know for sure too much about the chemistry in the lower layer of the epidermis—the germinating layer—that one might be eliminated. It would be a matter of dissolving keratin or some reduction of disulfide groups. But this might not be so in unhairing. It seemed not to be so in the old days with caustic soda. All we need is a straightforward proteolytic digestion. After what you have said, Dr. Pfannmuller, it pleases me to know that in Europe today there is a reversal of the old process—namely, not to swell the skins first. In some quarters that is thought to be bad, but that can be argued.

TITUS WEAVER (Ohio Leather Company): I cannot add anything as far as the enzyme unhairing is concerned, outside of the fact, for general information, that we have processed the skins that were enzymatically unhaired at Rutgers University by Dr. Nickerson. At present we are putting through the second set that he has unhaired. I will say that he has done a beautiful job of unhairing. I don't want to say anything about the quality of the leather as yet. But it has very good possibilities. The unhairing was complete.

Dr. PFANNMULLER: May I ask you what enzyme he used for unhairing? What was the origin of the enzyme?

MR. WEAVER: I don't know that. We are only processing the skins after he has unhaired them. These skins were unhaired at Rutgers University, and we processed the skins into finished leather.

AN INTRODUCTORY PSYCHOPHYSICAL STUDY OF BREAK IN LEATHER

I. DEVELOPMENT AND EVALUATION OF THE LEATHER GRAINOMETER*

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ABSTRACT

One of the most important characteristics of leather which concerns tanners and large consumers of leather is the property called break. Break is the system of wrinkles formed when the vamp of a shoe is flexed during walking. Since the number of the wrinkles is related to durability, appearance, and over-all grade of leather used in footwear, it is essential that this quality be carefully evaluated. The need for an objective method for evaluating break is especially emphasized by the failure of traditional visual, subjective inspection procedures to define or curb the use of coarse-breaking leathers in footwear. To solve this problem, an investigation of the break characteristic was undertaken. This work resulted in the development of an instrument called a Leather Grainometer. The instrument helped to define break objectively. Utilizing the Leather Grainometer, inexperienced personnel appear able to grade breaks more accurately and consistently than experienced commercial and technical personnel using the subjective, visual approach.

—x—x—

INTRODUCTION

Currently most leather grades are determined by expert opinion. It is assumed that the gradings reflect the consensus of the trade; however, when subjected to scientific inquiry, the selections of different veteran leather experts frequently are inconsistent. The current practice of grading leather employs over-all feel and appearance characteristics as prime criteria. Factors influencing serviceability and end-use requirements are of secondary consideration. However, for the military, these are the primary considerations;

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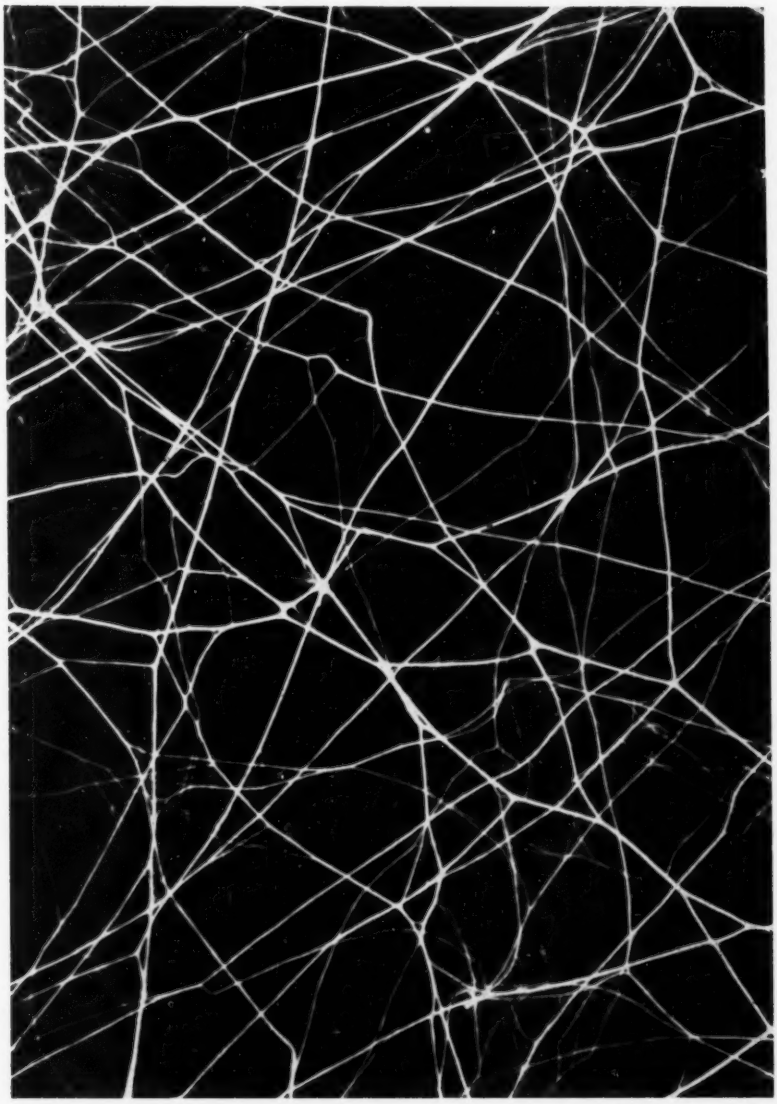

FIGURE 1.—Photomicrograph of elastin network of rat mesentery stained with resorcin-fuchsin, reproduced from the negative. It shows the branching character (anastomosis) of the elastic tissue, in marked contrast to the associated collagen (not shown). (Approx. ×450)

therefore, definitive standards and precise methods of evaluation are required. In the case of the Navy, where some degree of uniformity had been established among its leather inspectors, the maintenance of uniform standards has been complicated by the retirement of experienced inspectors and the subsequent employment of less experienced personnel.

One vital aspect of the problem of maintaining uniform standards for leather is concerned with the evaluation of a property called "break". Break is the formation of tiny wrinkles on the grain surface of leather when it is bent inward in a curve like that formed at the vamp of a shoe in walking. If the wrinkles are very minute, the leather is said to have a fine break; if the wrinkles are very large, the leather is considered to have a pipey or coarse break.

Fundamentally break is related to the nature of the fiber structure. Where leather breaks into many wrinkles, the fibers just beneath the grain merge well into the grain surface. The grain surface is relatively dense, and there is an intimate merging of the fibers of the grain and the corium. In coarse or pipey leather where the surface breaks into a few large wrinkles, the fibers beneath the grain are less subdivided, less intimately bound, and there is an obvious line of delamination. From the observations of Roddy (1) it may be concluded that the distribution of the elastic tissue fibers is perhaps the primary influence in the quality of the break. (*See* Fig. 1). He noted that the network of elastin fibers encompasses each follicle in the grain layer and that the fibers branch out in the corium. He also found that elastic fibers are more predominant in wrinkled areas and that the wrinkled areas are less thick from the grain to the flesh than neighboring smooth areas (2). Generally, younger cattlehides have proportionately more grain in relation to the corium and produce proportionately more wrinkles when indented than older stock. The closeness of wrinkles appears to be related to the energy of deformation (3), which in turn may be a function of the intimacy, quality, and quantity of the elastin network in the grain layer.

Functionally, a fine break is desired in leather because the manner in which leather breaks reflects the age, appearance, and serviceability of the stock. It has been frequently observed by the military that shoes made with pipey leather often split open at the vamp, whereas shoes fashioned from "tight" leather withstand rigorous wear. It is generally agreed throughout the shoe and leather industry that pipey leather is not as serviceable as tight leather.

Repeated inspection of stock oxfords worn by Navy personnel disclosed that shoes with coarse breaks were being accepted in the supply system. (*See* Fig. 2). A further study of the problem showed that although disallowed by the specification, pipey leather was insufficiently defined. As such, the acceptance or rejection of substandard leather was based on the feelings of the individual inspector or contractor. It was obvious that a more objective

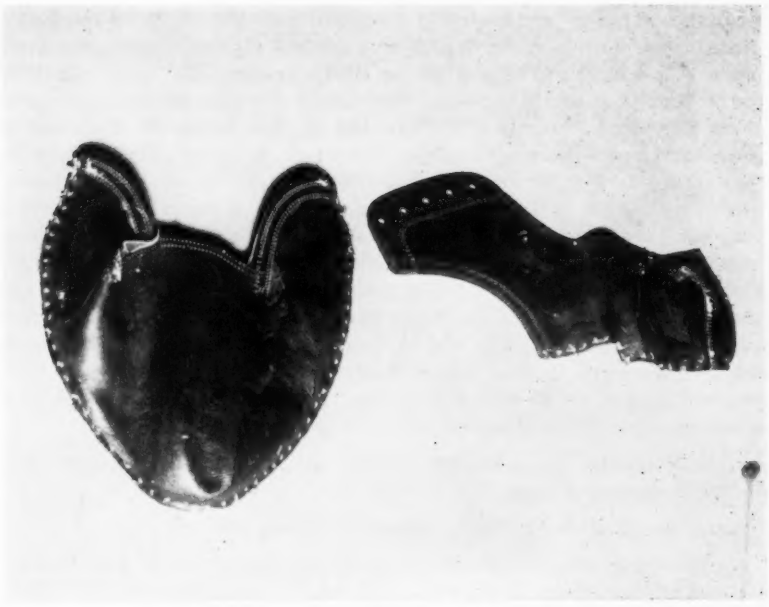

FIGURE 2.—Shoe upper parts with coarse break.

approach was needed to define break and that this method would have to be translated into numerical terms. The need was especially emphasized by Stubbings (4) who, referring to break and related properties, declared that to determine the effect of specific variabilities on resultant leather properties, more objective methods for measuring leather should be developed. Accordingly work began which aimed at

a. the development of a suitable definition of break,

b. the development of a measuring device that would translate the definition into terms lending themselves to definitive standards, and

c. the testing of the instrumental technique against the prevailing subjective method of judging break.

The work covered by this report discusses the realization of these aims.

DEVELOPMENT OF THE GRAINOMETER

A literature search disclosed that Wilson (5) had reported work on classifying break in 1929. He drew strips of leather tightly around a rod 3.2 mm. in diameter and designated the count of the resulting wrinkles as the break

measurement. This approach was consistent with the nature of the break characteristic and appeared to provide a concept capable of being rendered concrete as a more precise method for inspection purposes. This suggested the creation of an instrument that would bend a leather specimen precisely about a mandrel and hold it firmly. The wrinkles formed in the concave bend would have to be magnified, since fine creases are not readily visible with the naked eye. For purposes of information and refinement, this instrument would be expected to classify breaks into a number of objective levels. The basis for these levels would be established by comparison with the best technical tannery opinion. It was therefore planned to obtain graded sample leathers representing the opinions of the top sorters of the foremost calfskin tanneries. These standard specimens would again be graded by the instrument which would designate the objective grades. The specimens would then be submitted to shoe manufacturers and leather buyers and sellers who would examine them and designate their subjective grades. It was anticipated that this trial would provide data for

a. the setting up of quantitative break standards based on the best technical tannery opinion,

b. the testing of the reliability of the instrument, and

c. the comparison of instrument readings against subjective shoe factory and other commercial opinions.

The concept of break as defined above appeared adequate for operational purposes. The development of a suitable instrument, however, posed several technical problems. If a strip of leather was wound around a mandrel, the wrinkles were not readily visible. When the wrinkles were clearly observed, the position of the leather influenced the wrinkle count. Generally, manual clamping of the leather detracted from the precision of the method, consequently a two-part frame on the order of an egg slicer was devised. The upper part corresponded to a semicylindrical mandrel which depressed and curved the leather strip, and the bottom part contained a semicylindrical cavity for receiving the bent leather.

In the refined instrument that followed, the upper part, or cover plate, contained two semicylindrical bars, arc at 180°, radius 3/16″. (*See* Fig. 3). These two bars were mounted in line with each other, separated by a space to permit visual observation of the curved leather surface, and reproduced the effect of a continuous mandrel. The main body contained two retaining sides and a semicylindrical adjustable groove for receiving leathers of various thicknesses. (*See* Fig. 4). A regulating screw and dial cap with two main springs facilitated the groove adjustments. Four knurled nuts clamped the samples in place. An adjustable lens with a self-illuminating light source was mounted on the cover plate to illuminate and magnify the wrinkles. The finished instrument was called a Leather Grainometer.

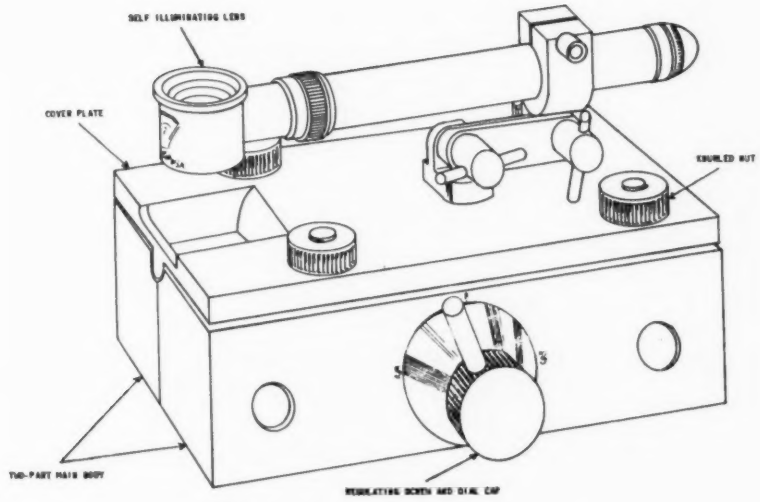

FIGURE 3.—Leather Grainometer (assembled).

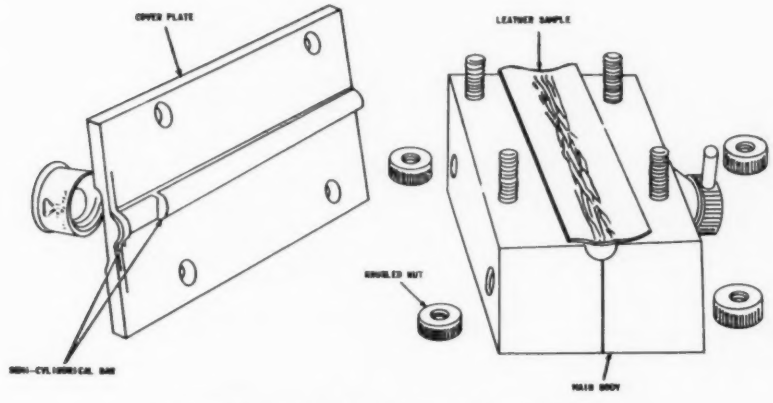

FIGURE 4.—Leather Grainometer (unassembled).

To operate the Grainometer, a user centered a 1½″ x 6″ sample on top of the main body and adjusted the groove to the thickness of the leather. He then fitted the cover plate over the specimen and depressed it into the groove. The cover plate was secured with four knurled nuts. The wrinkled specimen

was then examined, and the wrinkles were counted transversely with the aid of the self-illuminating lens. The wrinkles were counted over a span of 0.5893", determined by the 3/16" radius of the mandrel.

General testing with the initial Leather Grainometer showed that the principle and procedure were very satisfactory for the tannery and laboratory. Cut specimens could be evaluated in several minutes, and with the guide pins removed, the break of any section of a full side or skin could be determined without destroying the surface under examination. However, for the rapid quality control of vamps and quarters in the shoe factory, a quick clamping system was required; consequently, another model was designed for use by footwear inspectors.

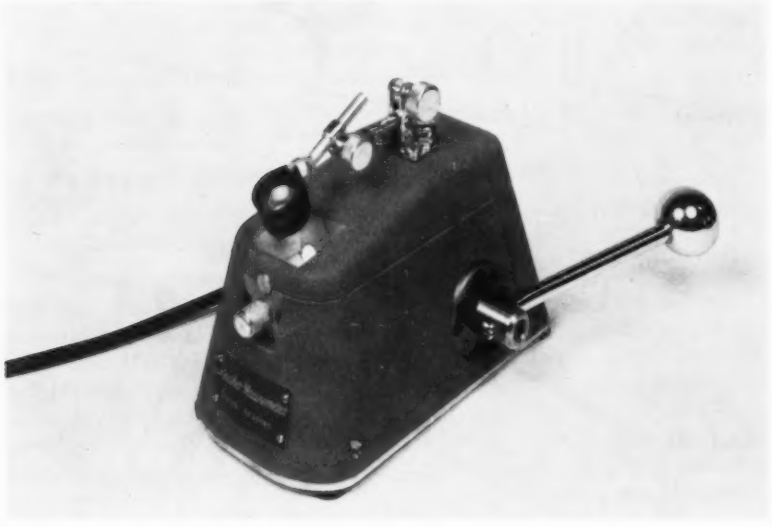

FIGURE 5.—Advanced Leather Grainometer.

The vamp model (*see* Fig. 5) had most of the essential dimensions of the Leather Grainometer. The later instrument's cover plate could be raised or lowered with the aid of a lever. Instead of a steel mandrel the new device utilized Lucite that permitted the piping of light into the cavity where the break appeared. Vamps, quarters, and other specimens could thus be locked into place with the turn of the lever, and the breaks of the different upper leathers could be immediately classified in the highly illuminated field. (*See* Fig. 6).

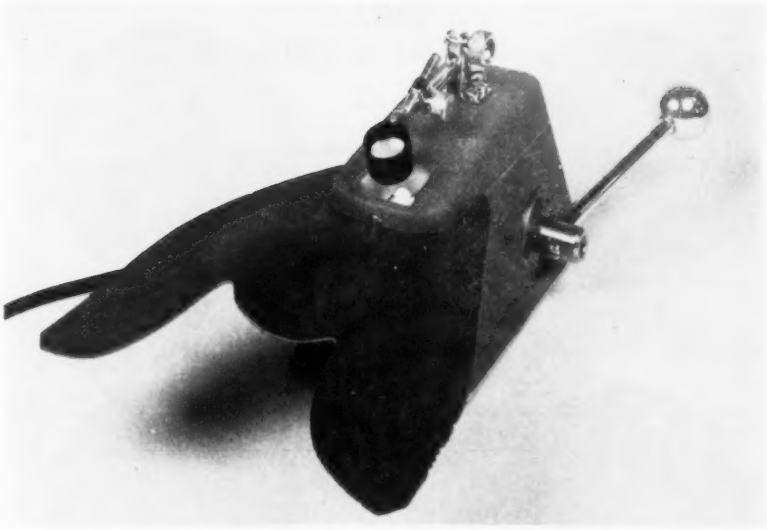

FIGURE 6.—Advanced Leather Grainometer with vamp sample.

STANDARDIZATION OF LEATHER GRAINOMETER

To standardize the Leather Grainometer the leather industry was consulted for opinions about the number of grades suitable for classifying break. The problem was discussed with technical personnel conversant with quality hides and skins. The technical opinions offered by these men and the range of wrinkles found in Navy upper leather indicated that the break characteristic could be subdivided into four groups, and these were called "fine" (group 1), "good" (group 2), "fair" (group 3), and "coarse" (group 4). When the designations were set, the four calf tanners supplying practically all of the Navy calf leather were solicited and requested to provide samples based upon the four levels of quality. The sorters of the tanneries, using their own concepts of break, provided a total of 34 samples representative of the four groups. These samples were then evaluated by the Leather Grainometer, and each specimen was assigned a wrinkle count which was columned in the group assigned by the tanner. The samples were checked several times by the author, then spot-checked by experienced technologists, and the results were found to be surprisingly consistent. The counts which are listed in Table I were averaged for each class of samples and showed that group 1 ("fine") had a mean of 20.7 wrinkles; group 2 ("good"), a mean of 17.1 wrinkles; group 3 ("fair"), a mean of 11.4 wrinkles; and group 4 ("coarse"),

TABLE I

BREAK GRADES OF SAMPLES SUBMITTED BY CALF TANNERS

	Fine (1)	Good (2)	Fair (3)	Coarse (4)
	Grainometer Count			
Tanner A	17	17	11	8
	17	16	12	7
	21	17	11	9
			14	7
Tanner B	21	17	12	9
	25	18	9	
		18	11	
			10	
			11	
Tanner C	26	17	—	6
Tanner D	18	18	11	10
			11	
			14	
Means	20.7	17.1	11.4	8.0

TABLE II

GRAINOMETER STANDARD

Adjective and Grainometer Equivalents

Numerical Grade	Adjective Grade	Grainometer Count
(1)	Fine	19 or more wrinkles
(2)	Good	15 to 18 wrinkles
(3)	Fair	10 to 14 wrinkles
(4)	Coarse	9 or fewer wrinkles

a mean of 8.0 wrinkles. (*See* Fig. 7). An analysis of variance showed that the means differed significantly at the one-percent level. The data provided a basis for setting up a range of wrinkle counts for the four adjective groupings. (*See* Table II). "Fine" breaks (group 1) showed 19 or more wrinkles; "good" breaks (group 2), 15 to 18; "fair" breaks (group 3), 10 to 14; and "coarse" breaks (group 4), 9 wrinkles or less. The ranked averages of the wrinkle count obtained from the instrument correlated perfectly with the ratings submitted by the top tannery experts.

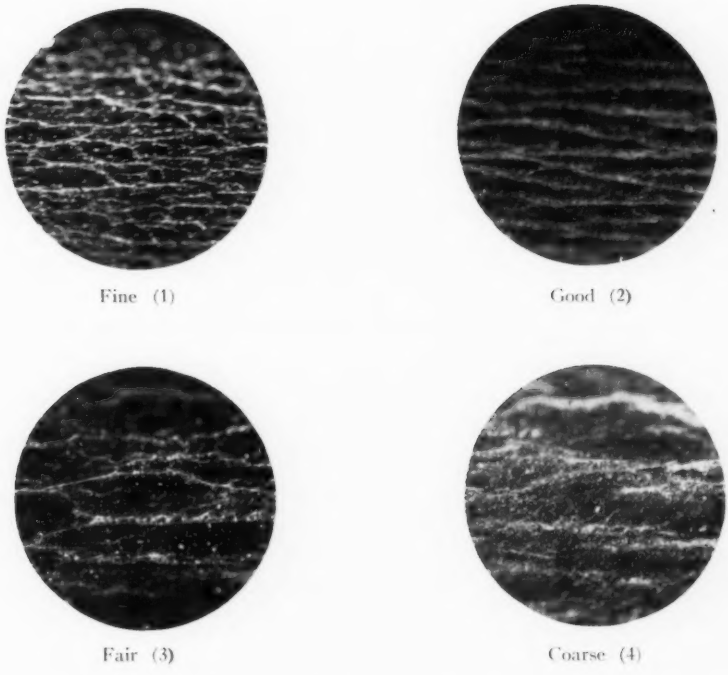

FIGURE 7.—Photomicrographs of four grades of break in calfskin. ×7

The results thus far provided a composite standard for checking the reliability of the Grainometer. The standard was based entirely on wrinkle counts taken with the Grainometer. A relatively small group of tannery sorters' ratings of individual samples differed slightly from ratings assigned by the Grainometer, and these ratings were reclassified to agree with the instrument. (*See* Table III). Thus if the machine gave a "good" rating to a specimen rated "fine" by a tanner, the machine rating prevailed. This arbitrary decision appeared necessary because there were some subjective grade overlappings in the "fine" and "good" categories. Some tanners selected "fine" samples with large wrinkle counts, while others selected "fines" that did not differ substantially from the "good" samples. The standard in effect ironed out these few differences between the major tannery experts. In this paper this composite standard is called the Grainometer Standard (Table II).

TABLE III

Sample No.	Fixed† Grainometer Counts	Fixed† Grainometer Grades	Expert Deviations from Fixed Counts	RATINGS BY INEXPERIENCED PERSONNEL EMPLOYING THE GRAINOMETER											
				Grainometer Counts				Grade Ratings*				Errors			
				Subjects				Subjects				Subjects			
				(S)	(G)	(F)	(C)	(S)	(G)	(F)	(C)	(S)	(G)	(F)	(C)
1	17	2	—	16	17	17	15	2	2	2	2	—	—	—	—
2	16	2	—	15	15	15	16	2	2	2	2	—	—	—	—
3	18	2	—	17	18	17	17	2	2	2	2	—	—	—	—
4	17	2	—	15	15	15	15	2	2	2	2	—	—	—	—
5	17	2	—	17	18	16	18	2	2	2	2	—	—	—	—
6	17	2	—	18	17	17	17	2	2	2	2	—	—	—	—
7	18	2	—	17	15	15	16	2	2	2	2	—	—	—	—
8	18	2	—	17	17	16	16	2	2	2	2	—	—	—	—
9	21	1	—	20+	20+	20+	20+	1	1	1	1	—	—	—	—
10	21	1	—	20+	20+	19	20+	1	1	1	1	—	—	—	—
11	26	1	—	20+	20+	20+	20+	1	1	1	1	—	—	—	—
12	25	1	—	20+	20+	20+	20+	1	1	1	1	—	—	—	—
13	17	2	+e	19	20+	20+	20+	1	1	1	1	+e	+e	+e	+e
14	17	2	+e	15	16	15	15	2	2	2	2	—	—	—	—
15	18	2	+e	19	20+	20	20+	1	1	1	1	+e	+e	+e	+e
16	6	4	—	5	4	5	4	4	4	4	4	—	—	—	—
17	9	4	—	9	9	9	12	4	4	4	3	—	—	—	+e
18	10	3	—	10	10	10	10	3	3	3	3	—	—	—	—
19	7	4	—	5	5	5	6	4	4	4	4	—	—	—	—

20	6	4	—	6	6	7	5	4	4	4	4	—	—	—	—
21	7	4	—	6	5	6	6	4	4	4	4	—	—	—	—
22	8	4	—	9	9	9	9	4	4	4	4	—	—	—	—
23	10	3	-e	11	12	13	11	3	3	3	3	—	—	—	—
24	12	3	—	11	12	12	12	3	3	3	3	—	—	—	—
25	11	3	—	14	14	14	15	3	3	3	2	—	—	—	—
26	11	3	—	10	12	10	10	3	3	3	3	—	—	—	+e
27	12	3	—	13	12	13	13	3	3	3	3	—	—	—	—
28	14	3	—	10	12	11	10	3	3	3	3	—	—	—	—
29	11	3	—	10	11	11	11	3	3	3	3	—	—	—	—
30	11	3	—	12	10	9	12	3	3	4	3	—	—	-e	—
31	14	3	—	14	14	14	15	3	3	3	2	—	—	—	+e
32	11	3	—	11	12	10	11	3	3	3	3	—	—	—	—
33	11	3	—	10	11	10	10	3	3	3	3	—	—	—	—
34	9	4	+e	9	9	8	6	4	4	4	4	—	—	—	—
			4+e			Upgrade errors					(+11e)	+2e	+2e	+2e	+5e
			1-e			Downgrade errors					(-1e)	-	-	-e	-
			5e			Total errors					(12e)	2e	2e	3e	5e

Mean Total Error $\frac{(12)}{4} = 3.0$

†Fixed grainometer counts and related grades represent correct readings as designated by author and trained technologists.
*1, 2, 3, 4 refers to "Fine", "Good", "Fair", and "Coarse" grades respectively.

CHECKING THE RELIABILITY OF THE GRAINOMETER

To check the reliability of the instrument, four persons who had no experience in leather were requested to grade the 34 specimens, using the machine. Their results showed a total of 12 errors or an average of 3 errors per person; the incorrect choices generally tended to upgrade the leather. (*See* Table III). The degree of error of the inexperienced subjects was limited. For example, no novice using the instrument misgraded a sample beyond an adjacent level, or 1 degree. A "fine" specimen (group 1) was misgraded and assigned to group 2. This was considered a negative error or downgrading of 1 degree. A "good" specimen (group 2) was misgraded and assigned to group 1. This was considered a positive error or upgrading of 1 degree.

The degree of error was chosen as a means of weighing mistakes. The maximum mistake possible was an error of 3 degrees positive or negative. If a subject misassigned a "fine" specimen (group 1) to the "coarse" group (group 4), he would have made a negative error of 3 degrees; if he upgraded a "coarse" specimen (group 4) to the "fine" group (group 1), he would have committed a positive error of 3 degrees. By way of interpretation, an error of 1 degree would be considered relatively minor, whereas errors of 2 degrees and 3 degrees would be considered proportionately more serious. The general results indicated that the gradings of inexperienced personnel were consistent and agreed substantially with each other and the Grainometer standard.

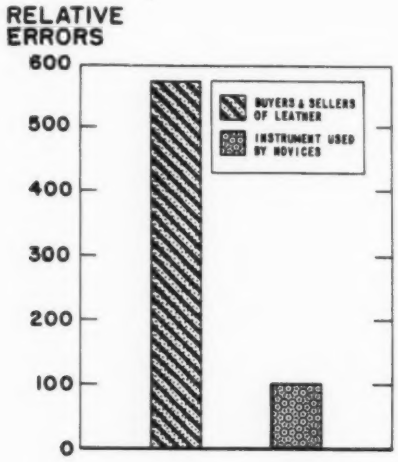

FIGURE 8.—Relative errors in judging break.

COMPARISON OF GRAINOMETER ACCURACY WITH SUBJECTIVE ACCURACY

The final test involved comparing subjective opinions rendered by seven experienced shoe manufacturers and bybuyers and sellers of leather (Table IV) with the objective results obtained by the inexperienced personnel using the Grainometer. The total subjective errors were 118, and the mean number of subjective errors per man was 16.9. The total errors of 2 degrees were 12. No errors of 3 degrees occurred.

When the above over-all average of the leather buyers and sellers was compared with the over-all average of the inexperienced personnel using the Grainometer, it was found that the experienced commercial graders made over five times as many errors as the inexperienced men using the instrumentation technique. (*See* Fig. 8). Figure 9 illustrates the number of errors committed by each participant in the evaluation. The best buyer-and-seller judge erred 11 times, while the inexperienced man with the poorest Grainometer score made 5 errors. He equalled the composite score of the professional sorters. Figure 10 shows the seriousness of the errors made by each subject. Leather buyers and sellers and shoe factory personnel in some instances were prone to misgrade "fair" samples of group 3 and assign them to "fine" group 1, which were errors of 2 degrees. No novices using the test device made errors of that magnitude.

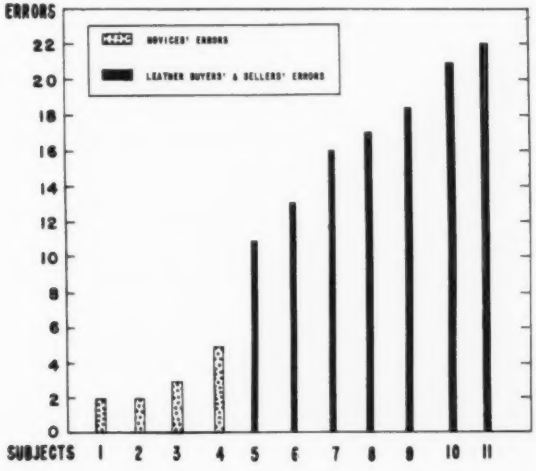

FIGURE 9.—Total errors in evaluating break.

TABLE IV

SUBJECTIVE RATINGS BY LEATHER BUYERS AND SELLERS

Sample No.	Grainometer Grades	Grade Ratings* Subjects (A)	(B)	(C)	(D)	(E)	(F)	(G)	Errors Subjects (A)	(B)	(C)	(D)	(E)	(F)	(G)
1	2	1	3	1	2	2	2	1	+e	-e	+e	—	—	—	+e
2	2	3	2	2	2	3	2	2	-e	—	—	—	-e	—	—
3	2	1	1	1	1	1	1	2	+e	+e	+e	+e	+e	+e	—
4	2	2	2	3	3	2	3	3	—	—	-e	-e	—	-e	-e
5	2	2	2	1	1	1	1	1	—	—	+e	+e	+e	+e	+e
6	2	2	2	2	2	2	2	3	—	—	—	—	—	—	-e
7	2	2	1	2	3	3	2	1	—	+e	—	-e	-e	—	+e
8	2	1	2	1	1	2	1	2	+e	—	+e	+e	—	+e	—
9	1	1	1	1	1	1	1	1	—	—	—	—	—	—	—
10	1	2	1	3	2	3	2	2	-e	—	-2e	-e	-2e	-e	-e
11	1	1	3	1	2	1	2	1	—	-2e	—	-e	—	-e	—
12	1	1	1	1	1	1	1	3	—	—	—	—	—	—	-2e
13	2	1	2	1	2	3	2	1	+e	—	+e	—	-e	—	+e
14	2	1	2	1	1	2	1	3	+e	—	+e	+e	—	+e	-e
15	2	2	1	3	2	3	3	4	—	+e	-e	—	-e	-e	-2e
16	4	4	3	4	4	4	3	4	—	+e	—	—	—	+e	—
17	4	4	4	4	4	4	3	4	—	—	—	—	—	+e	—
18	3	4	4	4	4	4	4	4	-e	-e	-e	-e	-e	-e	-e
19	4	4	3	4	4	4	4	4	—	+e	—	—	—	—	—
20	4	4	3	3	4	4	4	4	—	+e	+e	—	—	—	—
21	4	4	4	3	4	4	3	4	—	—	+e	—	—	+e	—

22	4	4	4	4	4	3	3	4	—	—	—	—	+e	+e	—
23	3	4	2	3	3	3	3	3	-e	+e	—	—	—	—	—
24	3	4	2	3	3	2	3	2	-e	+e	—	—	+e	—	+e
25	3	3	1	3	3	2	3	1	—	+2e	—	—	+e	—	+2e
26	3	3	2	4	3	1	2	2	—	+e	-e	—	+2e	+e	+e
27	3	3	2	1	3	1	2	4	—	+e	+2e	—	+2e	+e	-e
28	3	4	2	3	3	4	2	4	-e	+e	—	—	-e	+e	-e
29	3	4	2	3	3	3	3	4	-e	+e	—	—	—	—	-e
30	3	3	2	3	3	2	3	2	—	+e	—	—	+e	—	+e
31	3	3	2	2	3	2	3	1	—	+e	+e	—	+e	—	+2e
32	3	4	2	4	3	2	3	2	-e	+e	-e	—	+e	—	+e
33	3	3	4	4	4	3	3	4	—	-e	-e	-e	—	—	-e
34	4	4	2	4	3	3	4	3	—	+2e	—	+e	+e	—	+e
					+e—Upgrade Errors			(+70e)	+5e	+17e	+10e	+5e	+11e	+11e	+11e
					-e—Downgrade Errors			(-48e)	-8e	-4e	-7e	-6e	-7e	-5e	-11e
					e—Total Errors			(118e)	13e	21e	17e	11e	18e	16e	22e
					2nd degree "e", error of 2 grades			(12)	0	3	2	0	3	0	4
					3rd degree "e", error of 3 grades				0	0	0	0	0	0	0

Mean Total Errors $\frac{(118)}{7} = 16.9$

* 1, 2, 3, 4 refers to "Fine", "Good", "Fair", and "Coarse" grades respectively.

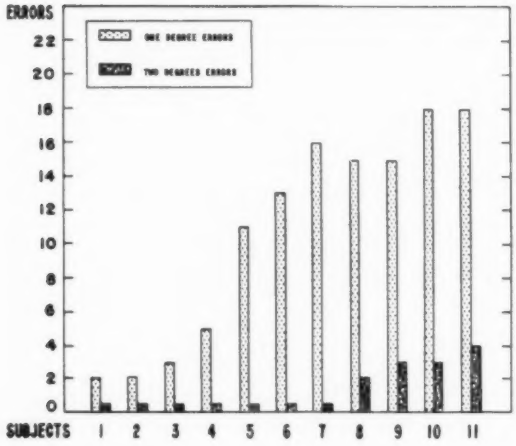

FIGURE 10.—Magnitude of errors in evaluation of break: instrument errors (subjects 1–4) vs. subjective errors (subjects 5–11).

SUMMARY

The results of this work indicate that an instrument defines the quality of break more accurately than the traditional subjective methods employed in the leather and shoe trades. Commercial personnel and even technical leather experts differ among themselves in the gradings of identical leathers; consequently, differences of opinion among the uninitiated are inevitable. By contrast, the instrumental technique assures consistent counts and gradings. Inexperienced men employing the Grainometer are able to grade leather breaks as well as or better than experts. The instrument also limited the degree of error and made possible an objective classification of break based on a table of wrinkle counts. Grainometer grading of break should replace subjective evaluations which are generally variable and inaccurate. Additional work may now be pursued to determine factors which influence break and relate the property to thickness, stiffness, follicle density, flexural fatigue, water resistance, and fiber structure. It is also planned to measure the subjective accuracy of tannery sorters against the instrument break standard.

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Received May 8, 1958.

DISCUSSION

MIETH MAESER (United Shoe Machinery Corp.): I have a couple of questions I would like to ask Mr. Bailey. First, he made a pretty strong statement here that break is definitely related to the failure of vamps in shipboard use. Before I came to this meeting, I checked with some people who have had more experience than I with this property in leather; I tried to find out if it were commonly known that pipey leather failed more quickly than non-pipey leather when used in shoe vamps. No one seemed to know that such was the case. I also conducted some flexing tests and was unable to find out whether or not it was true. My results were negative. I didn't deteriorate the leather, however. I would like to ask Mr. Bailey to discuss this point a little and see if anybody in the audience can express an opinion on it.

MR. BAILEY: We noticed in our work with shoes aboard ship, during continual evaluation with thousands of pairs of shoes, that, in general, there is almost an invariant relationship between cracking across the vamp and pipiness. The leather becomes wetted and dried repeatedly. We assume that it is a physical as well as chemical deterioration. In our experience pipey leathers crack across the vamps, whereas tight leathers do not. I might add that we noticed this cracking characteristic especially in degrained leathers regardless of treatment. We use a stuffed leather which is about five ounces in thickness for our work shoes, and these pipey sides from older animals crack very quickly in wear. They deteriorate much faster than our calfskin leather. We can say at once that our calfskin leather is a much better work shoe leather than our stuffed work shoe leather.

JOSEPH BASSETT (A. C. Lawrence Leather Company): I wonder if there is not still some personal judgment involved in using this instrument, bec use it seems to me there must be a certain number of wrinkles that do not necessarily go transversely. There may be some that go diagonally or even at right angles.

MR. BAILEY: The wrinkles are essentially parallel to each other as you will have observed in the illustrations of the photomicrographs. But I have charts pertaining to this paper which show that there is a surprising degree of consistency between the counts made by different individuals. The fact is

that those of us who were experienced and worked out the Grainometer count, or Grainometer standard, might have been arbitrary in our particular decision, but our possible inconsistencies were consistent. Among our inexperienced people, the errors or differences from the standard were consistent in the wrinkle-counting.

RICHARD C. CAMP (Marathon Corporation): Would a shoe made of leather with a pipey grain invariably crack in use? The reason I ask that question is that it is my understanding, based on not very much experience of my own, that pipey grain may be caused by any number of factors, leading from the beamhouse on through the fatliquoring. I was wondering whether pipey grain from whatever cause would be conducive to cracking across the vamp.

MR. BAILEY: Our experience leads us to believe that as a general rule when you have pipey leather subjected to extreme wear you will observe accelerated deterioration.

DR. TURLEY: I am not clear, Mr. Bailey, on this: In carrying out the tests with the Grainometer instrument, was it a small area of a vamp that was measured? And then, when the leather was judged by sorters, did they judge whole skins? It seems to me you cannot make much of a comparison there. But perhaps I didn't get the story right.

MR. BAILEY: The sorters or tanners provided us with swatches for evaluation. An absolute determination was made on the swatches, and our results did not refer to the classification of a total skin. It was an area—a very small area. As far as the vamp judgments are concerned, they were done on small areas of vamps. There does not seem to be too much variation over a small area as far as break is concerned.

JOSEPH ORIETAS (Albert Trostel & Sons, Co.): Have you reached any conclusions as to the minimum number of wrinkles that would be accepted by the Navy?

MR. BAILEY: Well, we have an opinion. For example, we have an opinion that about seven wrinkles—and I think this is liberal—would be minimum for the acceptance of kips and calfskins.

MR. ORIETAS: And in considering locations, what location would that be?

MR. BAILEY: We think that the best thing to do for control purposes would be to evaluate vamps, and for general purposes to evaluate the skins. But I think it is more important to evaluate the cut part, vamp, or quarter. In other words, pinpoint your pipiness. And that is why we went ahead and developed the vamp control or vamp model of the Grainometer. For skin evaluation, we would recommend the test areas indicated in Federal Specification KK-L-311.

MR. GROTA (Rueping Leather Co.): Were the swatches which were submitted by the tanners the same pieces which were then evaluated by the Grainometer?

MR. BAILEY: Some of the swatches were four inches by eight inches. And they were of a particular grade. What we did was chop them up so that they would fit the particular instrument. But we kept the classifications that the tanners had assigned to them.

MR. GROTA: Then the subjective tests by the tanners, and the Grainometer test, were done on the same leather pieces?

MR. BAILEY: That is correct.

MR. GROTA: Another question: You stated the number of wrinkles on pipey leather to be approximately seven or fewer. I was just curious, in listening to the talk, as to what sort of a reading we might get from a leather like shell cordovan, for example, which is considered extremely tight and smooth?

MR. BAILEY: I think that is one of the exceptions. We were essentially concerned with calfskin. All of the work, the grading, and all of these tables, relate to calfskin. I think for another type of skin or another type of animal hide, you would have to develop another set of standards.

C. DAVID WILSON (Rueping Leather Co.): Is the classification of excellent, good, fair, and poor, which was used as a reference in assessing the errors of the instrument and of the experienced operators the original tanners' classification as an absolute standard or a choice of borderlines with the instrument?

MR. BAILEY: The tanners' classification was converted into a wrinkle-count classification. The sorters' classification was essentially the same as the wrinkle-count classification which became the standard that was set up.

MR. WILSON: With a small degree of error?

MR. BAILEY: With a small degree of error. We set up a table on the basis of that classification, and we gave it to people who were inexperienced. Then we had them make the count and make the grade assignment based on their wrinkle counts.

MR. WILSON: In other words you picked out borderlines which more or less maximized the tanners' opinions as to what the borderlines should be?

MR. BAILEY: No, we were not arbitrary about it. We tested these groupings by an analysis of their variances, and their means differed significantly at the one-percent level.

FRANK ZEISSIG (Hiteman Leather Co.): If you had a coarse break on one type of tannage and a fine break on another, would you say that both would go to pieces in the same way? In other words, is it independent of tannage?

MR. BAILEY: I cannot answer that, because we were working exclusively with chrome-tanned calfskin leather.

MR. SALAMATOV: Tanned according to the specifications of the Navy?

MR. BAILEY: Yes.

MR. SALAMATOV: Then for this particular purpose those measurements were all right, but wouldn't it be risky to conclude that they would be satisfactory for any other kind of leather?

MR. BAILEY: We would not recommend this particular minimum wrinkle count for any type of leather, but we would develop other applicable minimums.

THIS WE BELIEVE!

A young man who attended an interview for an important scientific job . . . was asked to sign a contract on the dotted line. The conversation then went like this:

"Why do you put two crosses?"

"I can't write. I've been so busy in the lab that I never learned."

"Then what does the first cross stand for?"

"Oh, that's my name—John Smith."

"Then why is there a second cross?"

"That means Ph.D."

—*The New Scientist*, May 15, 1958.

WANTED: A PRAYING MANTIS

The cockroach *Diploptera punctata* has a brace of glands which secrete a mixture of *p*-benzoquinone and two of its derivatives. Because it ejects this fluid when disturbed, T. Eisner of the biology department at Cornell figured the phenomenon might be defensive. And so it turns out.

Writing in *Science*, Eisner says he left roaches open to attack by such predators as carabid beetles, praying mantises, lycosid spiders, and ants. All of them went after the roaches at once, but the quinone spray (ejected immediately upon attack) drove off the ants and carabids, who stumbled a bit during departure, sometimes losing their ability to walk altogether; this loss of coordination seldom lasted more than two minutes. Spiders were repelled (though only by larger nymphs and adults), but showed no loss of coordination. Praying mantises don't seem to mind the spray at all.

—*Chemical and Engineering News*, August 11, 1958.

THE NATURE OF THE NEUTRAL SALT EFFECT IN CHROME TANNING*

II. EFFECT OF SODIUM CHLORIDE ON THE REACTION OF BASIC CHROMIUM SULFATES WITH COLLAGEN

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INTRODUCTION

The present paper deals with a system with components of different anions, i.e., solutions of basic chromium sulfates containing increasing amounts of sodium chloride. In comparison with the system previously discussed (1), which contained components with a common anion, it offers additional complications due to the formation of mixed salts and protolysis products as well as mixed acido-chromium complexes.

The chromium sulfate–sodium chloride system is of importance in practical tanning, since common salt is carried over into the tanning bath by the pickled stock, and more salt commonly is added to the chrome tanning bath as a swelling-depressing agent. Actually, that is the main function of the neutral salts in technical chrome tannage. The aim of this paper is to show how added neutral chlorides, represented by sodium chloride, affect the composition of the chromed collagen, the chrome-collagen compounds formed, and some properties typical of chrome leather. Since the effects of addition of neutral chlorides to solutions of basic chromium sulfates on the H-ion concentration of the system, on its alkali stability (precipitation figure), and on the tanning effect as evaluated by the hydrothermal stability (boiling test) are well established, these aspects will only be considered in instances that are directly applicable to the present problem. It suffices to recapitulate the salient points of these effects.

PRESENT STATUS OF THE PROBLEM

The research groups of Wilson and Thomas (2), the pioneers in this field, have shown that the H-ion concentration of solutions of basic chromic sulfate is increased by the addition of neutral chlorides (3), and also that

*For the first paper of this series on the system: chromium sulfates–sodium sulfate, *see JALCA*, **45**, 536 (1950). The present paper summarizes the results of researches carried out in collaboration with Mr. Magne Nestvold, Research Scholar of the Norwegian Research Council, 1950–51, and part of earlier and later work of the senior author.

the chromium salt is made more stable toward alkali (4), that is, by the addition of salt, basic chromic sulfate solutions can be brought to a higher basicity without precipitating. Wilson (5), as well as Thomas and Foster (6), noted that neutral chlorides decrease the fixation of chromium by collagen. The increased H-ion concentration of the solutions resulting from the addition of neutral chlorides was considered to be the main cause of the impaired chrome fixation. However, Thomas and Foster (6) suggested also that the chlorides form complex compounds with the chromium sulfate, rendering it less active in combining with the skin protein. Wilson (5) also believed that some penetration of the anion of the neutral salt into the chromium nucleus was involved in the neutral salt effect.

In an important paper in 1920 Wilson and Gallun (7) showed that leather tanned in solutions of basic sulfates containing large amounts of neutral chlorides did not stand the ordinary "boiling test", in contrast to the leather tanned in solutions containing only the commercial basic sulfate. This was, indeed, the first demonstration of the effect of neutral salts on the real tanning property as measured by hydrothermal stability. The amount of chromium combining with the collagen is by no means a measure of the tanning potency, although this figure is important theoretically. It was further shown by Thomas and Foster (6) that this neutral salt effect is rather slight in very dilute or very concentrated solutions of the chrome tanning salt, whereas a marked effect is found in solutions of moderate chromium concentrations.

In unpublished investigations by the senior author, partly mentioned in passing in reviewing this field (8, 9), it has been established that the effect of sodium chloride on the chromium fixation and the tanning power of solutions of basic chromium sulfates is rather slight at low basicity. With increasing basicity the effect becomes more pronounced, being very drastic on the extremely basic chromium sulfates. Further, it has been shown by the ion-exchange technique (10) that the formation of noncationic (mainly nonionic) chromium complexes is favored by the addition of large amounts of sodium chloride to solutions of basic chromium sulfates. It has also been stressed that the very marked difference between the effects of sodium sulfate and sodium chloride on the hydrothermal stability of chrome-tanned leather suggests that the composition of the chrome-collagen compound formed plays a governing role (11). Thus, of two leather specimens of the same chromium content, tanned by the same 67%-acid chromium sulfate, the one tanned in the solution made 1.5*N* in sodium sulfate withstood the boiling test, while the specimen tanned in the solution which had been made 1.5*N* in sodium chloride shrank to 45% of the original area. The difference in stability remained after the neutralization of the leather specimens (pyridine treatment) (12). In view of the fact that leather containing such large amounts of chromium as 8–10 Cr_2O_3 per 100 collagen would not stand the test, even after the removal of its ionic acid groups, it is evident that the

failure of leather that had been tanned in solutions of basic sulfates containing high concentrations of sodium chloride to stand the boiling test was due neither to insufficient amounts of combined chromium nor to higher percent acidity of the fixed chromium compounds. According to the senior author's findings (13), mainly unpublished but mentioned on passing in résumés (8, 9), the main cause of the impaired tanning power of basic chromium sulfates induced by the addition of sodium chloride is the displacement of ionically held sulfate and part of the sulfato groups in the cationic chromium complexes by the chloride; a decrease in cationic chromium complexes probably is involved also. In the present paper some typical results from investigations forming the basis for this view will be presented.

EXPERIMENTAL

Solutions of chromium sulfate.—Solutions of 67%-acid chromium sulfate, free from neutral salts, corresponding to the empirical formula: $Cr_2(OH)_2(SO_4)_2$, were used for the main series with hide powder as the substrate, in order to avoid the added complexity of sodium sulfate which is present in the ordinary type of commercial chromium sulfate used for tanning. The stock solution was prepared by reducing a mixture of equimolar parts of chromic acid (CrO_3) and sulfuric acid by hydrogen peroxide, which was added slowly to the cooled solution as described in another connection (14). A similar type of neutral salt-free 67%-acid chromium sulfate was obtained by reducing the CrO_3–H_2SO_4 mixture in concentrated solution at the boil with sucrose, adjusting the rate of addition of the reducing agent and other conditions so as to maintain a violent reaction, practically excluding the formation of secondary acidic oxidation products. Upon analysis of the ensuing stock solutions for Cr, total sulfate, and hydrolyzable sulfate, the acidity percentages agreed within 1% (66% and 67%). For the tanning experiments with pelt an ordinary chrome liquor was used, since the tanning of pelt in solutions of chromium sulfate devoid of swelling-depressing neutral salts is often complicated by the swelling of the pelt in solutions of low chromium content. This phenomenon and the anomalous effects that it produces in studies of the neutral salt effect on chromium sulfates were first noted by Otto in his Dissertation (15). This chrome liquor was prepared by reducing a solution of sodium bichromate (250 g. per l. of $Na_2Cr_2O_7 \cdot 2\ H_2O$) with sulfur dioxide, and removing the excess of sulfur dioxide by boiling, which also is required for decomposing any anionic complexes (tetrathionate and sulfite) formed (16). Solutions containing 0, 1, 2, and 4 moles of NaCl per l., at a final Cr concentration of 0.4*N* (10.2 g. per l. of Cr_2O_3) were prepared, and aged for at least two months prior to use. In some series the various solutions were boiled two minutes, cooled, and left for two months to attain equilibrium.

Analysis of the solutions.—The amounts of Cr, total sulfate, hydrolyzable sulfate, sodium, and chloride present in the solutions were estimated. The composition of the chromium complex was determined by the ion-exchange column technique employing the cation exchanger Dowex-50, operating in the sodium cycle (17), and the anion exchanger Amberlite IRA-400, used as the hydrochloride (18), according to procedures described earlier (10). Apparently it is not generally recognized that in solutions of high neutral-salt content the use of the *acid* form of a cationic exchange resin results in large errors on estimating the content of noncationic chromium complexes. The likely explanation is the reaction of the freed protons with the noncationic chromium complexes, which are converted into positively charged complexes (19). Hence, operation in the sodium cycle is important.

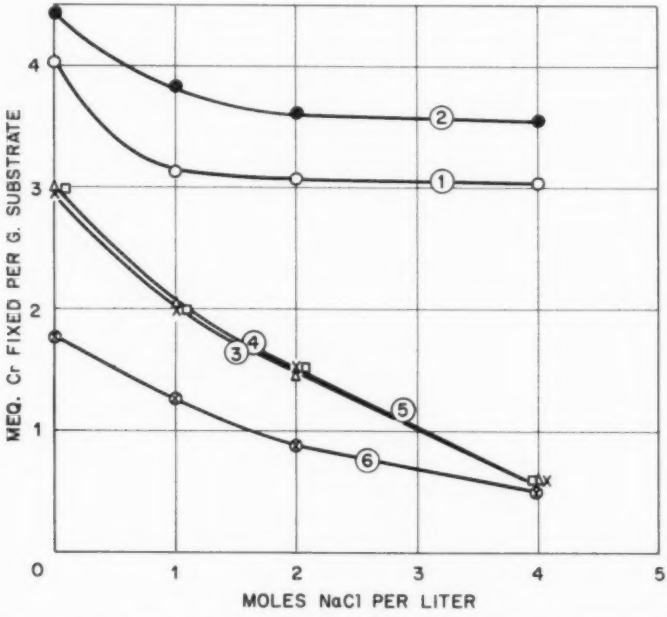


FIGURE 1.—The fixation of chromium from solutions of 67%-acid chromium sulfate by various cation exchangers as a function of the sodium chloride content of the solution.

1. Hide powder
2. Amberlite-IRC-50 (Na salt)
3. Dowex-50 (Na salt)
4. Amberlite IR 120 (Na salt)
5. Amberlite IR 120 (NH_4 salt)
6. Wofatit KS (Na salt)

Some results from experiments in which an excess of chromium was allowed to react with the sodium salts of cation exchangers of both the sulfonic acid and carboxylic types (20), by shaking the resin with the solutions, are recorded in Fig. 1. This mode of interaction (21) is similar to the technique used in chrome tanning. It gives a measure of the preferential fixation of chromium by the substrates. The electrochemical nature of the solutions was ascertained by ionophoresis on paper by a method described earlier (22).

Mode of tanning.—In the hide powder series, 6.00-g. portions of Lyon hide powder (5.40 g. of collagen) were treated with 100-ml. portions of the solutions of the chromium sulfates for periods of from 5 days to 5 weeks. The tanned hide powder was separated from the residual solution on a glass filter and lightly washed. The chromed stock was then shaken twice for 10 minutes, with 100-ml. portions of water. The residual solution combined with the washings was made up to 500 ml. In the experiments with calfskin pelt, portions of 30.0 g. of lightly pressed pelt (limed, unhaired, and delimed) (=10.4 g. of collagen) were shaken for 9 to 11 days with 100 ml. of the solution of the chromium sulfate, 0.4*N* in Cr.

Analytical methods.—The residual solutions, combined with the washings, were analyzed for Cr, total sulfate, and acid sulfate. By subtracting these values from those of the original solutions, the amounts of Cr and SO_4 fixed by collagen were determined indirectly. Some of the series were run in duplicate; in others half of the chromed substrate, after a light washing as described for removal of sorbed solution, was dried for analysis without further treatment. The other half of the substrate was shaken for two hours in 200 ml. of 4.0% pyridine solution. After washing and shaking out with two 100-ml. portions of water, the residual pyridine solution and the washings were combined. The total acid content of the solution was ascertained by titration to pH 8 with 0.1*N* NaOH solution. Sulfate was determined as $BaSO_4$. Portions of the solution were also taken to dryness, ashed at 500°C., the ash dissolved, and the content of Cl determined. In the dried chromed hide powder the contents of ash, Cr, combined sulfate, combined chloride, and collagen (N × 5.56) were determined. The results are stated in terms of meq. per g. of collagen. Only in the first series (Table II) are the data expressed in the traditional percent on the dry substance, since the final statement in meq. of reactant combined with 1 g. of the protein is scientifically a more satisfactory way of expressing the results.

The degree of stabilization imparted to the collagen by the various solutions was determined by the boiling test. The degree of shrinkage of the area of the original specimen after immersion for two minutes in boiling water was measured (23). Since the shrinkage temperature was 100°C. or higher in practically all instances, the decrease in area on boiling gives a better and more practical indication of the tanning effect than the shrinkage

temperature. The use of nonaqueous solvents for measuring shrink temperatures over 100°C. often yields misleading results.

RESULTS

The data from the separation of the cationic and anionic chromium com-

TABLE I

EFFECT OF NaCl ON THE COMPOSITION OF CHROMIUM COMPLEXES IN SOLUTION

No.	Moles NaCl per Liter	pH	% Cations	% Uncharged Complexes	% Anions	% Acidity of Cationic Sulfato-Cr Complexes
1	0	3.17	92	8	0	32
2	1	2.87	86	12	2	32
3	2	2.64	80	18	2	30
4	4	2.35	71	25	4	31

plexes by percolation of the solutions through columns of the cation exchanger Dowex-50 and the anion exchanger Amberlite IRA-400 are given in Table I. For this series the hydrogen peroxide–reduced, 67%-acid chromium sulfate ($Cr_2(OH)_2(SO_4)_2$), not heated before aging, of final concentration 0.4*N* in Cr, was used.

The mean value of the acidity of the sulfato-chromium cations was 32% for solution No. 1 of Table I, determined by the indirect method. By using the resin of the quaternary base–type, Amberlite IRA-400, in the form of the nitrate, the acidity was found to be 33% by applying the technique described earlier (18). All the added Cl ions were recovered in the filtrate, proving the absence of chloro-complexes. These data show that the formation of nonionic chromium complexes is favored by the addition of sodium chloride to the solution of pure basic chromium sulfate ($Cr_2(OH)_2(SO_4)_2$). A slight amount of negatively charged chromium complexes is also formed.

It was found on ionophoresis on paper that increasing salt addition tended to increase the small fraction of nonmigrating chromium, in agreement with the findings by the ion exchange.

The series of ion-exchange studies which simulated the conditions of the chrome-tanning process was carried out by shaking for 1 hr. portions of the sodium salt of the hydrated cation exchange resin in quantities equal to 1.0 g. of dry substance with 15.0 ml. of the solution of 0.4*N*, 67%-acid chromium sulfate. The filtrates and combined washings were made up to 200 ml. and analyzed for Cr and total sulfate. The amount of chromium and sulfate fixed was obtained by difference. The results are shown in Fig. 1 in which the curve for the chrome fixation by hide powder (tanned 7 days) is inserted for comparison.

TABLE II

COMPOSITION OF CHROMIUM COMPOUNDS FIXED BY HIDE POWDER FROM SOLUTIONS OF 67%-ACID CHROMIUM SULFATE OF INCREASING SODIUM CHLORIDE CONTENT

Solution No.	I	II	III	IV
NaCl, moles per l.	0	1	2	4
From analysis of chromed hide powder:				
% on dry substance:				
Ash	8.6	6.9	7.0	7.2
Cr_2O_3	8.5	6.8	6.8	6.8
Combined sulfate (as SO_4)	8.98	4.81	3.22	2.10
Combined chloride (as Cl)	0.00	1.89	3.20	3.94
Collagen (N × 5.56)	82.5	85.0	87.9	88.6
Cr_2O_3 per 100 collagen	10.3	7.95	7.15	7.67
% Acidity of chrome-collagen compounds				
SO_4	58	36	24	16
Cl	0	22	35	41
Total	58	58	59	57
Meq. fixed per g. collagen:				
Cr	4.07	3.14	3.06	3.02
Combined SO_4				
In Cr complex	1.36	0.69	0.55	0.48
In ionic linkage	1.02	0.46	0.20	0.00
Total	2.38	1.15	0.75	0.48
Combined Cl				
In Cr complex	0.00	0.28	0.40	0.42
In ionic linkage	0.00	0.40	0.67	0.82
Total	0.00	0.68	1.07	1.24
Total anions in ionic linkage	1.02	0.86	0.87	0.82
% Acidity of acido-Cr complex fixed (pyridine method)				
SO_4	33	22	18	16
Cl	0	9	13	15
Total	33	31	31	31
By difference from analysis of original and residual solutions:				
Meq. Cr fixed per g. of collagen	4.10	3.07	2.92	3.01
Meq. SO_4 fixed per g. of collagen	2.45	1.19	0.77	0.47
% Acidity of Cr-sulfate fixed	60	39	26	16

Table II contains the data from the series in which hide powder was tanned with the solutions of the 67%-acid chromium sulfate free from neutral salts. At this point it will be sufficient to call attention to the good agreement between the directly determined values of the amounts of chromium and sulfate fixed by collagen and the acidity of the chromium sulfate–collagen compounds, and the indirectly obtained values (from the analysis of the solutions). The results will be commented on in the Discussion and are shown graphically in Fig. 2.

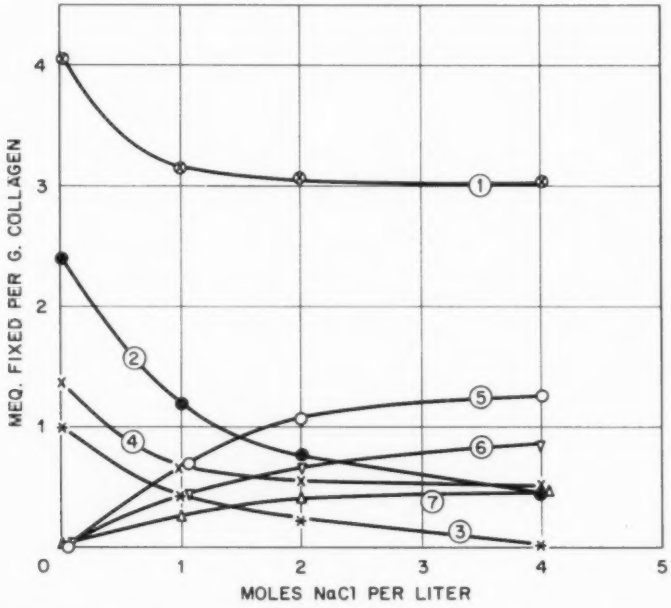


FIGURE 2.—The distribution of chromium and anions of the chromium-collagen compounds as a function of the sodium chloride content of the solution of basic chromium sulfate.

1. Cr
2. Total SO_4
3. SO_4 in ionic linkage
4. SO_4 in the chromium complex
5. Total Cl
6. Cl in ionic linkage
7. Cl in the chromium complex

The essential data from a typical experiment with pelt are presented in Table III. 30.0 g. of lightly pressed pelt (=10.4 g. of collagen) was tanned

TABLE III

COMPOSITION OF CHROMIUM COMPOUNDS FIXED BY PELT FROM SOLUTIONS OF 67%-ACID CHROMIUM SULFATE OF INCREASING SODIUM CHLORIDE CONTENT

Solution No.	I	II	III	IV
NaCl, moles per l.	0	1	2	4
Meq. fixed per g. collagen:				
Cr	3.24	2.84	2.77	2.80
SO_4	2.00	1.01	0.75	0.44
Cl	0.00	0.71	0.73	1.18
% Acidity of chrome-collagen compounds:				
In the form of SO_4	62	35	27	16
In the form of Cl	0	25	26	42
Total	62	60	53	58
Ts in °C.	>100	>100	100	98
% Shrinkage of area in boiling test (2 min.)				
Directly	0	19	45	51
After pyridine treatment	0	15	38	47

for 11 days with 100 ml. of solution of the salt-free, 67%-acid chromium sulfate containing 10.2 g. Cr_2O_3 per l. The pelt was limed, unhaired, delimed, and brought to the isoelectric point before tanning.

The results by the indirect method (from analysis of solutions) for fixed chromium in meq. of Cr per g. of collagen were: 3.25, 2.86, 2.75, and 2.79, in excellent agreement with the values obtained by direct analysis of the chrome leather. For the fixed sulfate the figures in meq. were: 1.93, 0.97, 0.73, and 0.39.

The results obtained in the corresponding series with pelt tanned with solutions of an ordinary sulfur dioxide–reduced chrome liquor are given in Table IV. The time of tanning was 8 days. The uptake of Cr, Cl, and SO_4 is shown graphically in Fig. 3.

In the following discussion the effect of the treatment of chromium sulfate–tanned leather with 2*M* and 4*M* solutions of sodium chloride, as documented in earlier papers (23), will be considered. In this connection the results from a hitherto unpublished experiment will be summarized. Hide powder which had been tanned with the 67%-acid salt-free chromium sulfate at a concentration of 1*N* Cr was washed. Part of the chromed hide powder (=5.0 g. of collagen) was shaken with 100 ml. of 2*M* sodium chloride for 24 hr. This treatment was repeated thrice with fresh salt solution. Finally it was shaken

TABLE IV

THE EFFECT OF SODIUM CHLORIDE ON THE TANNING OF PELT WITH 67%-ACID CHROMIUM SULFATE LIQUOR

Solution No.	I	II	III	IV
NaCl, moles per l.	0	1	2	4
Meq. fixed per g. of collagen:				
Cr	3.60	2.92	3.08	3.24
SO_4	2.16	1.02	0.86	0.65
Cl	0.00	0.76	0.93	1.33
% Acidity of chrome-collagen compounds:				
In the form of SO_4	60	35	28	20
In the form of Cl	0	26	30	41
Total	60	61	58	61
Ts in °C.	>100	>100	>100	100
% Shrinkage of area in boiling test:				
Directly	0	0	25	40
After pyridine treatment	0	0	22	37

for 3 consecutive times with 100 ml. of 4*M* sodium chloride, 24 hr. each time. No sulfate was found in the solutions subsequent to the first extraction with the 4*M* sodium chloride solution. Table V shows the composition of the original and the salt-treated chromed hide powder specimens.

Evidently the sulfate anions and also the sulfato groups are completely displaced on repeated extraction of the chromium sulfate–collagen compounds with concentrated solutions of sodium chloride. Remarkably, simultaneously with the sulfate displacement, a considerable loss of irreversibly fixed chromium occurs, amounting to some 10% of the chrome content of the original chromed hide powder. This indicates that the strength of some of the valency forces involved in the binding of the sulfato-chromium complexes to the protein is impaired by the salt treatment and moreover that the chloride complexes formed are less firmly attached to the collagen than the ordinary cationic sulfato-chromium complexes.

DISCUSSION

The data in Table I show that with increase in the concentration of sodium chloride the formation of nonionic chromium complexes is markedly augmented. On analysis of the filtrate from the cation-exchanging column, the total amount of chloride ions added was recovered. Thus, no formation of complexly held Cl groups had taken place. Against this negative statement

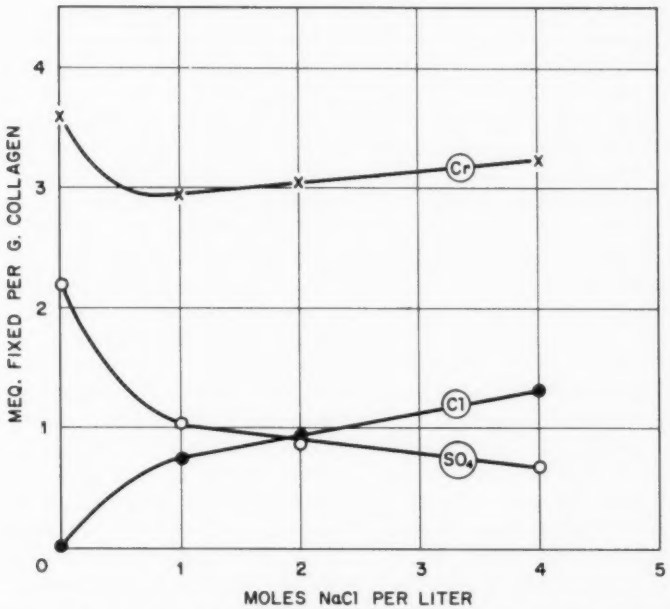


FIGURE 3.—The fixation of Cr, Cl, and SO_4 by pelt from solutions of 67%-acid chromium sulfate as a function of sodium chloride content.

1. —×—×—×— Fixed chromium, Cr
2. —○—○—○— Combined sulfate, SO_4
3. —●—●—●— Combined chloride, Cl

TABLE V

EFFECT OF REPEATED TREATMENT OF CHROMIUM SULFATE–TANNED HIDE POWDER WITH SODIUM CHLORIDE SOLUTIONS

	Original Stock %	NaCl-treated Stock %
Ash	8.9	8.8
Cr_2O_3	8.8	8.6
Combined SO_4	10.2	0.0
Combined Cl	0.0	2.1
Collagen	80.1	87.4
Cr_2O_3 per 100 collagen	11.0	9.8
% Acidity of chrome-collagen compounds:		
SO_4	61	0
Cl	0	16
Total	61	16

stands the finding of complexly held Cl groups in the collagen chrome-tanned with the solutions containing added sodium chloride. This apparent contradiction is probably to be explained by the different state of combination of the chromium complexes existing in the solutions as ionic species, on one hand, and those present in combination with collagen, held principally by covalent forces, on the other hand. In the latter instance the covalent-bound form of chromium very likely manifests an entirely different valency distribution from that of chromium in the electrovalent state. It has been pointed out in other connections by the senior author (24) that the usual form of the protolytic equilibrium based on proton discharge from the aquo groups of the hexa-coordinated chromium cation is not applicable to the hydrolysis of chromium complexes present in covalent attachment to the collagen such as those in the chrome-collagen compounds, since a free anion is necessary for the compensation of the freed proton.

The anion series, expressing the complexing affinity of the various anions for chromium (25), has been derived from the study of ionic reactions and systems. Hence, this arrangement may not necessarily be applicable to the coordinate-covalent linkage of chromium in the chromed collagen. Therefore, it appears to the authors that the denial of the existence of Cl groups in oxo-chromium complexes combined with collagen is not justified from theoretical considerations. It is worthy of note that the consensus of the findings is that the Cl group is not complexly bound in ordinary basic chromium chlorides of the cationic type in dilute solutions. This fact has been established by a number of investigators (26), including the senior author (27), by different methods. However, it should also be emphasized that the existence of chloride residues as chloro-groups in collagen tanned with basic chromium chlorides has been unequivocally established experimentally (28). At the same time, it is worthy of mentioning that the degree of stability of these chloro-groups generally is very much inferior to that of the sulfato-groups. In some instances the majority of these complexly bound Cl groups are displaced on prolonged washing.

In the present instance it is found (Table II) that from the solution with the highest concentration of sodium chloride, the collagen binds cationic chromium complexes in which about half the complexly bound sulfate groups of the ordinary basic chromium sulfate have been displaced by Cl groups. It is also evident from the results of the analysis of the hide powder tanned in the chrome bath 4*M* in sodium chloride that the chrome complexes fixed by collagen contain on the average one equivalent of Cl and one equivalent of SO_4 per two atoms of chromium. Thus, in this instance the chloro-sulfato-oxo-chromium-collagen complexes possess complexly bound Cl groups which even resist a two-hour treatment of the stock in 4.0% solution of pyridine (pH 8.2) and the subsequent washing procedure. This aspect of the composition of the chromium complexes fixed by collagen from solutions with

varying content of sodium chloride will be discussed later on. Since the present results also have some bearing upon the question of the existence of chloro-oxo-chromium complexes in combination with collagen, the findings of Table II have already been referred to in this context.

According to the graphs on the chrome fixation by the various resins used in the ion-exchange series (Fig. 1), the best agreement with the general tendency of the chrome uptake by collagen from the solutions concerned is shown by the resin with the carboxylate ion as functional group (Amberlite IRC-50) (20). The sulfonic acid-type of resin shows a decidedly greater decrease in the chrome fixation from the solutions of high chloride concentration than the decrease shown by collagen (17, 20). The relatively low complexing tendency for chromium of the charged sulfonic acid group compared to the carboxylate group gives a satisfactory explanation of the different trend. For the electrochemical differentiation and for the complex analysis of chromium salts the sulfonic acid-type of exchanger is more suitable than the carboxylate resin. The reason is that the high complexing power of the carboxyl ion introduces additional complications, its action not being limited strictly to the positively charged chromium complexes. This is particularly important if the straight ionic reactions are to be evaluated.

It should be noted that the heavy decline in the chrome fixation by the resins induced by increasing the sodium chloride concentration of the solutions of the basic chromium sulfate, which also applies to additions of sodium sulfate, is not due to the introduction of compensating sodium ions in the form of these neutral salts. The evidence for this statement has been presented in earlier papers (17, 20). The main cause is the shift of the equilibrium between cationic and noncationic complexes in favor of the uncharged chromium complexes, which are not able to react with the ion exchangers.

The main problem of this investigation centers around the data presented in Tables II–IV. It is evident from Table II that the protolytic equilibrium of the solutions of the basic chromium sulfate is shifted in the direction of increased formation of hydrochloric acid by the increase of the ionic strength of the solutions as to the Cl ion. From the data obtained by analysis of the specimens of the chromed hide powder before and after the treatment with pyridine, as well as from the estimation of the amounts of Cl and SO_4 ions in the residual pyridine solutions, it is evident that the quantities of Cl ions which are associated with the cationic protein groups and present as counterions, attached to the fixed chromium complexes with surplus positive charges, increase rapidly with augmented neutral-salt concentration. Finally, it is found that all the anions taken up by collagen from the solution of chromic sulfate made $4M$ in sodium chloride are Cl ions. This effect has nothing to do with any Donnan equilibrium, the establishing of which is out of question at the neutral-salt concentrations used. It is probably a result of the increased ionic strength of the chloride in the systems.

It should be noted that in the ionic attachment of the chloride both the cationic groups of the collagen and the surplus positive charge of the fixed chromium complexes are involved. While the number of sulfato-groups in the chromium complexes decreases gradually with increasing Cl ion concentration, as is the case with the SO_4 ions also, the incorporation of the Cl group into the fixed chromium complexes grows steadily until about half the sulfato-groups of the original sulfato-complex of the solutions are displaced. It has been observed earlier by the senior author (29) and by Merrill and Niedercorn (30) that about half of the complexly bound sulfate groups of ordinary chrome leather, i.e., one equivalent SO_4 on two atoms of chromium, are very firmly held. An explanation for the unusual stability of this portion of the sulfato-groups is that they function as bridges between two chromium atoms. It is remarkable that in spite of these radical constitutional alterations of the chrome-collagen compounds, which result from the action of the chloride, the amount of chrome fixed by collagen is very little affected. Of course, the increased H-ion concentration, which implies fewer carboxylic ions of the collagen, tends to reduce the chrome uptake by the collagen also. Much more deep-going and far-reaching, however, is the effect of the added sodium chloride on the degree of stabilization that is brought about by the reaction of the chromium complexes with the skin protein, as is evident from the results of the boiling tests (Tables III and IV).

As an introduction to the comments on the data obtained in the tanning of pelt, it should be stressed anew that in such systems, as well as in practical chrome tanning, the effect of neutral salts on the swelling and the physical state of the hide structure is of governing importance. Thus, in the absence of swelling-depressing salt in the solutions of chromium sulfates (Table III), the pelt will swell in the initial stage of chrome fixation. This will retard the diffusion of the chromium salt through the interior of the pelt and impair the tannage. By the addition of small amounts of sodium chloride (0.2*M* sodium chloride suffices) the chrome fixation will be greater than in solutions free from neutral salt. Moreover, the distribution of the fixed chromium complexes will be more uniform throughout the interior of the skin. Although the series of Tables III and IV are not strictly comparable in some respects, it should be noted that of the two solutions which do not contain sodium chloride (No. 1 in the respective tables) the one (in Table IV) containing one mole of sodium sulfate per mole Cr_2O_3 gives a leather of greater chrome content than the neutral salt-free solution (No. 1 in Table III).

It was demonstrated in the early work of Wilson and Thomas (2) that by very heavy addition of salt the chromium uptake by collagen tends to be increased again. This is also shown by the figures for fixed chromium in Table IV and Fig. 3. It is well known that sodium chloride markedly increases the chromium fixation by collagen from solutions of basic chromium

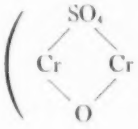
chlorides (31). In the present instance the increased chrome uptake from the solutions made 4*M* in NaCl probably is due to the effect of the sodium chloride on the sulfato–chromium chloride formed under these conditions.

As to the composition of the chrome-collagen compounds formed in the experiments with pelt (Table III), the findings parallel those of the hide powder series (Table II). The anions combined are mainly Cl ions, and a marked displacement of complexly bound sulfate groups and penetration of Cl groups into the chromium complexes have taken place. A remarkable feature is that the chromium uptake has only been reduced by some 10–15% of the amount fixed by collagen from the solution devoid of salt by making the tanning solution 4*M* in NaCl, while the degree of hydrothermal stability of the leather obtained in this instance is radically impaired. The "boil-proof" leather of the straight sulfate tannage (No. 1) is changed into a leather which shrinks by 40% in area after tanning in the chrome bath containing 4*M* NaCl. On the other hand, by making the solution of the 67%-acid chromium sulfate 2*M* in respect to sodium sulfate, the chromium uptake is cut down to half of the value obtained in the salt-free solution. However, the hydrothermal stability of the resulting leather is not detrimentally affected, since this leather resists the action of boiling water (8, 9). This contrary behavior of the two systems and the leather specimens produced is maintained after neutralization of the leather; hence, the difference is not accounted for by different acid contents of the specimens. The composition of the acido-chromium complexes in the differently tanned leather specimens, particularly the extent of the penetration of the Cl group into the chromium nucleus, appears to govern the stability of the chrome-collagen compounds obtained in tanning with cationic chromium complexes.

It is known from earlier work (23) that when ordinary chrome leather (chromium sulfate tannage) that does not shrink in the boiling test is immersed for a few days in 2–4*M* sodium chloride, complete displacement of the ionic sulfate takes place, and about half of the total of sulfato-groups present in the original leather are removed. The final result is a drastic labilization of the leather, as shown by an area shrinkage of the order of 30–50% in the boiling test. This fact adds further support to the view advanced of the importance of the composition of the fixed chromium complexes for the cross-linking of the elementary units of collagen as the primary factor in this neutral-salt effect.

As noted earlier, and as demonstrated by the data in Table V, complete displacement of the sulfate groups directly attached to the chromium atoms in chrome leather occurs on repeated treatment of chromed hide powder with 2–4*M* sodium chloride. Concomitantly an appreciable loss of irreversibly fixed chromium is noted. This indicates the rupture of some valency forces between the chromium complexes and the collagen, induced by this radical

salt treatment. It should be noted that for labilization of the chromed collagen, the breaking of only one link in the bipointly fixed chromium complex should be necessary. The shift of the bipoint fixation of some chromium complexes in the direction of a more pronounced unipoint attachment to the collagen, with lowered degree of cross-linking, may well be induced by the mass action effect of the sodium chloride on the cationic chromium complexes.

This problem is intimately connected with the distribution of the anions of the chromed collagen between the protein and the chromium complexes. Those chromium complexes that are not completely discharged by the carboxyl ions of the collagen will carry surplus positive charges which have to be balanced by the anions. Hence, by estimation of the number of equivalents of anions per atom of chromium functioning as counterions in the fixed complex, the percentage of the chromium fixed which is present in bipoint and unipoint combination with the collagen can be evaluated (32). Such an approximation has been attempted, apparently yielding reasonable results, for systems with the bifunctional  cation, which can form

either one or two links with the carboxylic ions of collagen (32). The method (33) is based on the fact that a fair assessment of the protein-bound acid is obtained by equilibration of the chromed collagen with water of pH 5.0 and that all the anions including those functioning as the counterion to the fixed chromium complex can be estimated by equilibration at pH 8. An absolute requirement, however, is the complete inactivation of the carboxyl groups of the collagen by the chromium complexes. In the present instance any such approximation is not feasible, since the last-mentioned criterion is not fulfilled. Another mode of approach is the estimation of the number of free basic groups of collagen by determining the uptake of 0.1*N* hydrochloric acid on very brief interaction with the substrate (10 minutes). On account of the possible interaction of the added acid with the chrome complexes, brief treatment is essential. When the total amount of anions held by the chromed collagen is known, the protein-attached portion can be obtained by difference. However, this technique has not yet yielded the required information. The problem is still subject to further investigation.

It appears to the authors, particularly with regard to the observed displacement of the irreversibly fixed sulfato-chromium complexes by sodium

chloride, that the final explanation of the present neutral-salt effect is to be found in the alterations of the cationic sulfato-chromium complexes by the mass action effect of the sodium chloride. Thereby, the cross-linking of the collagen units is impaired, particularly by the diminished facility of the chromium complexes for multipoint attachment to adjacent polypeptide chains or helical units of the collagen lattice. However, the only safe conclusion to be drawn from the available information and the data presented is that by addition of sodium chloride in large quantities to the tanning bath of basic chromium sulfates, the main effect is the displacement by the chloride groups of sulfate ions and complexly bound sulfate groups commonly present in leathers of ordinary tannage with basic sulfates.

SUMMARY

The effect of addition of sodium chloride to solutions of basic chromium sulfates on the composition and the hydrothermal stability of the chrome-collagen compounds (chrome leather) is as follows:

As the concentration of Cl ions increases, the collagen shows preferred affinity for them. A more or less extensive displacement of sulfate anions takes place. In solutions 4*M* in chloride, the sulfate which exists in ionic combination in the chromed collagen is displaced completely. The complexly fixed sulfate groups show greater resistance to displacement by the neutral chloride; however, about half the sulfato groups are displaceable. A marked impairment of the hydrothermal stability of the leather is the most characteristic result. Since the decrease of the chrome fixation induced by the added salt is rather small, it is believed that this detrimental effect is caused by the changes taking place in the chromium complexes on the penetration of Cl groups, which changes impair the ability of the complexes to cross-link and stabilize the protein. A shift of the reaction in the direction of a greater number of chromium complexes combined unipointly with collagen is suggested to be the governing factor.

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LIFE LINES

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MILTON BAILEY supervises footwear development for the U. S. Navy Clothing and Textile Office. His contributions include a washable fur tannage, the water-resistant fleet shoe, a nonsolvent sole leather impregnation technology, and the Leather Grainometer. He conducts the seminar in shoe and leather technology at the New York City Community College of Applied Arts and Sciences. Before assuming his current position, Bailey was plant manager of Ruderman, Inc. His education includes a B.B.A. and M.S. from the College of the City of New York. He is an honor graduate of Pratt Institute School of Leather and Tanning Technology. He joined ALCA in 1952 and has been active in the Joint ALCA-ASTM Leather Committee.

DR. THEONE C. CORDON received his B.S. and M.S. degrees from Utah State University and his Ph.D. from Rutgers University. He was associated with the New Jersey Experiment Station and the University of Idaho before becoming affiliated with the Eastern Regional Research Laboratory of the U. S. Department of Agriculture where he has conducted research on hides, tanning materials, and leather since 1942.

ALFRED L. EVERETT is a graduate of Lehigh University, Bethlehem, Pa., receiving his degree in 1940. After almost five years in the Army he joined the staff of the Eastern Regional Research Laboratory, U. S. Department of Agriculture, in 1946. Since 1947 he has been concerned with research on hides and skins at the same location, now known as the Hides and Leather Laboratory, Eastern Utilization Research and Development Division. For the past several years he has conducted histological studies as part of the program on developing a process for enzymatic unhairing of hides.

DR. K. H. GUSTAVSON—See the August, 1957, *Journal*.

OBITUARY

GERARD KEVIL

We have been advised that Gerard Kevil of International Shoe Company died suddenly very recently. Mr. Kevil joined ALCA in April, 1948, as an associate member and became an active member in December, 1957. The Association extends its sincere sympathy to relatives and friends.

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ABSTRACTS

Thermal Shrinkage of Collagen in Solutions of Electrolytes. W. G. Crewther and L. M. Dowling. *J. Phys. Chem.*, **62**, 678–84 (1958).—Measurements were made of the rate of shrinkage of kangaroo tail tendons, at 50° and 60°C., at pH values from 2 to 12, in solutions of various salts. Time in minutes for 50% shrinkage was determined. The pH values were controlled by 0.1*M* buffers, and the kind of buffer salt used had some influence on the results, but such effects are believed to be small compared to those of the much higher concentrations of neutral salts that were employed. The tendons were soaked 24 to 60 hr. at 2°C. in the test solutions before carrying out the determinations. At 50°C. in the absence of added salt (other than the 0.1*M* buffer) the tendons shrank instantly at pH values 2 to 4 and 11.5 to 12, and showed no perceptible shrink at pH values 6 to 10. At 60°C. measurable rates of shrink were found at all pH values except 9. Shrinkage tests at 50°C., in 1*M* NaCl, NaBr, NaI, LiCl, LiBr, LiI, KBr, KI, and CaI_2, showed in general that the salts retarded shrinkage both at low and high pH values and accelerated shrinkage at intermediate pH values. Tests with various concentrations of salt up to 3*M* showed that rate of shrinkage increased with salt concentration at pH 9, but at pH 2 the rate of shrinkage decreased to a minimum and then increased with further increase in concentration. These effects, and specific effects of individual salts (which are very marked), are explained by the assumption that anions are adsorbed preferentially at the protein-solution interface, thereby decreasing the positive, or increasing the negative, charge on the protein, thus lowering the thermal stability of the protein at pH values above the isoelectric point and increasing it at pH values on the acid side. Adsorption of the anions varies inversely with hydration of the anion and directly with hydration of the cation. The shape of the shrinkage curves indicates that shrinkage is not simply the conversion of native to denatured collagen by a first-order reaction. The units of structure of the collagen are converted to the denatured form in a random manner by a first-order reaction, but the denatured units are initially prevented from contracting completely by the rigidity of the residual native collagen.

H.B.M.

Measurement of the Modulus of Elasticity as a Factory Control Method. G. Tóth, V. Pósa, and J. Kerese. *Das Leder*, **9**, 56–61 (1958).—Measurements of bending elasticity with a modified Schopper tester have been used for 4 years for factory control. To obtain consistent results the following conditions were essential: (1) the relation between thickness of test specimen and span must be constant; (2) bending must continue until the 2 specimen ends are at an angle of 90°; (3) the load must be applied to the flesh side; and (4) the specimen must be bent at least 20 times before testing. Specimens were taken in the location specified for tear specimens, calculating the number of specimens by the formula $0.7\sqrt{n}$ (but not less than 10.) Specimens were 4–5 cm. wide and 40 times as long as thick. After being conditioned for 24 hr. at 65% relative humidity, they were bent through 180° around a cylinder whose diameter was 25 times the leather thickness, bending 20 times with the grain and 20 times with the flesh out. Measurements on wet leather were made in the same manner after first soaking for 25 hr. in 5 volumes of water at 20°C. For testing, the

specimen was supported by 2 rollers held in a frame attached to the upper jaw of the tester. The distance between rollers was adjusted to 25 times the thickness of the leather (less 0.71 d, where d is the diameter of the rollers). The load was applied to the center of the specimen by means of a roller attached to the lower jaw of the tester (speed 15 cm/min), and the load was increased until the ends of the specimen were at an angle of 90° with each other, or until the specimen slipped through between the rollers. Several tests were made on each specimen and averaged. The modulus was calculated from the formula

$$E = \frac{1.9\,P\,l^3}{a\,b^3}$$

where P is load, l is span, and a is width, and b is thickness of specimen.

Results of about 10,000 measurements are summarized. Standard deviations, based on results for 1 month, were about 20% for dry and 30% for wet specimens. Control by the modulus made it possible to supply leather of just the firmness desired by the purchaser. There was good agreement between the modulus and subjective quality grade. In many cases leathers with a high modulus were more resistant to abrasion than those with a low modulus but not always. Important conclusions regarding quality, origin, and method of manufacture of sole croupons can be derived from data for modulus by bending. The relation between the moduli of elasticity by bending, by stretching, and by compressing was investigated. The modulus by stretch was greatest for all types of leather, that by compression lowest, and that by bending intermediate. The compression modulus, however, increased with increasing pressure, a phenomenon related to porosity. The modulus of the flesh layer was much higher than that of the grain layer. Higher bending loads were therefore needed for a given strain when the load was applied to the grain than to the flesh surface of a specimen because the flesh layer has less stretch. Of the 3 elasticity measurements, that by bending was most rapid and therefore was best for control work. I.D.C.

The Configuration of Polypeptide Chains in Proteins. R. B. Corey and L. Pauling. *Ibid.*, **B**, 249–67.—The object of this paper is to show how precise dimensions obtained experimentally from simple substances can be used together with fundamental structural principles to derive probable configurations for the polypeptide chain that are so precisely defined that they can be critically evaluated by direct experiment. The derivations of two helical configurations and of the pleated sheet configurations are described. There is strong evidence that the α-helix is a fundamental structural component of certain synthetic polypeptides and of α-keratin and other proteins of the α-configuration. The antiparallel-chain pleated sheet has been found to represent the arrangement of the polypeptide chains in *Bombyx mori* and Tussah silk fibroins. The parallel-chain pleated sheet may well be the structural basis of the β-keratin proteins, but its presence has not been confirmed by comparion of observed and calculated X-ray pattern. Author's summary.

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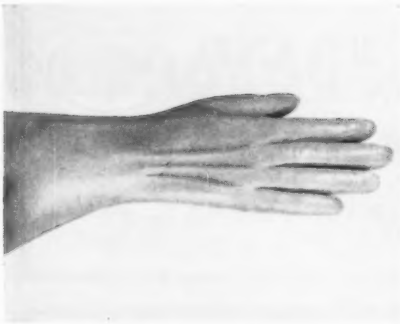

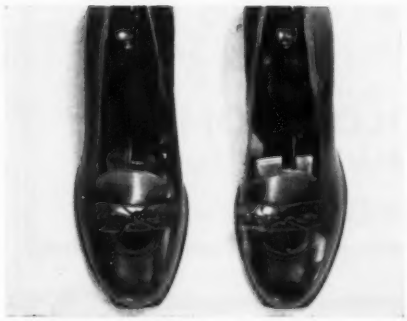

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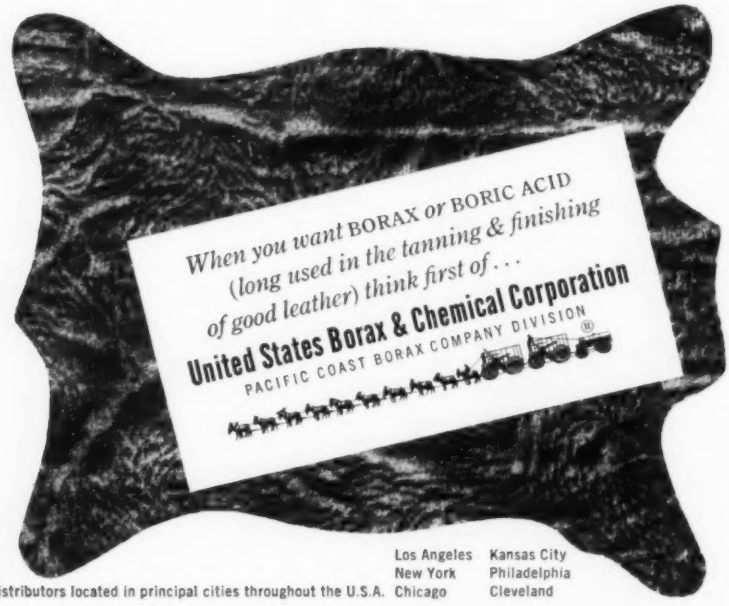
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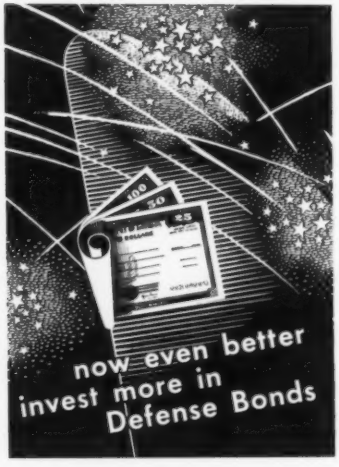

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Chicken Farmer Tells Why Egg Yolk Varies From Batch to Batch--Recommends Synova

A few weeks ago a down-east chicken farmer threw new light on an old tanning problem. He was asked why he didn't encourage his hens to lay egg yolks that were uniform from month to month.

His answer may be old stuff to oldtime tanners. "Nothin' I do ever changes their feeding habits," he confided. Then he added some helpful advice, "Eggs is fer eatin' and Synova's fer tannin'." A suggestion that makes good sense to many modern tanners.

Synova is Uniform

For Synova is a true egg yolk synthetic that is absolutely uniform from batch to batch and from season to season. By using uniform Synova, tanners are able to upgrade their leather on the table.

Synova has long storage stability too. Every supply drawn from warehouse has precisely the same properties as every other. This saves time, upgrades stock. Another time saver . . . Synova can be used at temperatures up to 130°F., eliminating chill floating and door changing.

And plenty of money is saved as Synova is equivalent to a 5½c egg yolk . . . goes four times as far too. Costs run 22% less. Freight, handling and storage are cut by 75%. Stock can be held in sammy without mold.

Try a Sample

Sounds like a tall order for ANY fatliquor. And maybe it is. Yet all these advantages offered by Synova have been proved over and over again by profit-minded tanners.

Perhaps you're now using natural egg yolk or a "replacement" and want to improve your leather and sweeten your profits. Then modern Synova is meant for you. Try it on a no-risk basis. Let us ship you a trial sample. Write or phone today.

It's time you switched to Synova!

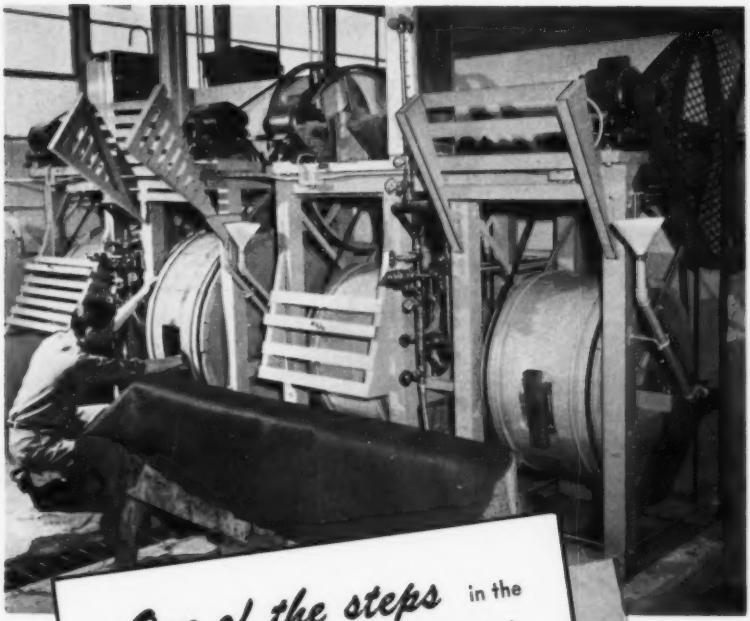
SEABOARD CHEMICALS, INC.

Dept. 10D, 30 Foster St.

Salem, Massachusetts

In Canada: Tennant Union, Ltd., Toronto

Overseas Export: Wolff International, Inc., Milwaukee, Wisconsin, U. S. A.



One of the steps in the successive screening of new chemicals is the application for tanning in these drums using full size skins or sides. This provides the quantities of leather necessary for physical and chemical testing.

CHEMTAN COMPANY
EXETER, NEW HAMPSHIRE

CHEMTAN COMPANY
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All our facilities are devoted exclusively to the tanning industry